Study of Interfacial Reactions in Metal-Silicon and Related Systems by High-Resolution Electron Microscopy and Thermodynamic Analysis

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This article discusses means for investigating and understanding the stability or reactivity at interfaces important in semiconductor processing. It is shown that high-resolution electron microscopy is capable of, and indeed essential to, phase identification at the nano-scale level. The interpretation of interfacial stability can be based on a phase diagram approach. However, as the number of elements involved at a single interface increases, then higher order phase diagrams are required. A method for deriving such diagrams is described and examples to illustrate their application are given. Emphasis in this paper is placed on metal-silicon based systems particularly Ti-Si, Ti-Si-O, Ti-Si-N and Ti-Si-O-N, and related silicide-forming elements.

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I. Introduction

As the dimensions of solid-state integrated circuits become increasingly small (*e.g.* $0.3\ \mu\text{m}$ for 64M bit DRAM's) the atomic structure at critical interfaces plays a more influential role on the electronic properties and performance. The manufacture of such devices involves many processing steps, a large proportion of which takes place at elevated temperatures. In addition it is expected that the fabricated "chip" should maintain its integrity during prolonged service, while mild heating occurs locally by resistive flow of electrical current. It is important therefore to provide a means of understanding the stability or, alternatively, the reactivity at interfaces involved in semiconductor microelectronics, and, since the dimensions involved are on the nano-meter scale, to recognize that high-resolution electron microscopy (HREM) is the best method for structural characterization at this level. Metallurgical thermodynamic considerations, using equilibrium or metastable phase diagrams, comprise the necessary framework for approaching this problem.

Metal-silicon interfaces are obviously a necessary component of silicon-based circuits, because electrically conducting contacts must be made to the semiconductor. In this article, the application of thermodynamic principles for such systems will be described. It will be seen that HREM is extremely powerful in revealing the nature and extent of any interfacial reaction and that the interpretation of the results can be based on the phase diagram method. Simple contacts can involve an elemental metal with the elemental semiconductor, which can have basic scientific interest also. From a metallurgical point-of-

view, their understanding can start with the binary phase diagram. Increasing complexity, by the involvement of additional elements (*e.g.* alloy contacts on silicon, elemental contacts to compound semiconductors such as gallium arsenide), can be incorporated through ternary and higher-order phase equilibria.

II. Experimental Procedures

Thin-film metal deposition onto a semiconductor substrate can be achieved by several means. In our work we have relied primarily on sputter or electron-beam deposition schemes, with the semiconductor surface cleaned by standard chemical etching methods. Specific conditions are described in the original literature citations. Alternatively, multilayer samples can be fabricated which increase significantly the volume of "interfacial material" available for study. Cross-section microscopy is essential for showing the nature or absence of any interfacial interaction but through-foil work provides complementary information and is especially powerful for diffraction investigations. High-resolution microscopy is performed following now well-established procedures (*e.g.* (1)), in our case employing a Philips EM430ST instrument with 0.2 nm resolution. Careful specimen preparation is critical to the success of the experiment: we use the technique described by Bravman and Sinclair⁽²⁾.

III. Results and Discussion

1. Binary systems

The simplest combination involves an elemental metal and an elemental semiconductor (*e.g.* Al-Si, Ti-Si). Since we are typically interested in a metal thin film on

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Fig. 1 Equilibrium binary phase diagrams for important silicon metallization systems: (a) Ti-Si, (b) Al-Si (Ref. (3)).

the semiconductor substrate, the overall composition of the system is weighted towards the latter. Annealing induces a reaction, the products of which can be predicted from the binary phase diagram (e.g. (3)) if equilibrium is reached. There tends to be two major types of systems (Fig. 1): those in which compound formation is favored (e.g. Si with Ti, Mo, W, Co, Ni, etc.) and those in which a eutectic diagram occurs (e.g. Si with Al, Au, Ag). In the former case, annealing the metal on a silicon substrate will produce the most silicon rich silicide. Since the resistivity of such compounds can be quite low (e.g. in the range $10\text{--}100 \times 10^{-8} \Omega \cdot \text{m}$), they can be useful themselves as contact materials⁽⁴⁾. Most notable are the disilicides of titanium, tungsten and cobalt. In some cases epitaxy can be achieved and the atomic arrangements at the interface deduced from high-resolution images (e.g. (5), (6)). For non-silicide forming elements, mutual dissolution will occur to achieve solid solution saturation at the annealing temperature, the most well-known example of which brings about the "spiking" phenomenon in aluminum-silicon contacts⁽⁷⁾.

The path to equilibrium need not be straightforward and metastable phases can be formed prior to the equilibrium compound (e.g. C49 TiSi₂ before C54

TiSi₂⁽⁸⁾, hexagonal MoSi₂ before tetragonal MoSi₂⁽⁹⁾). The final product tends to have the lowest resistivity and so is more useful technologically. However one of the more interesting recent observations concerns the *production of an amorphous phase* upon interdiffusion at the interface. Since this can occur on deposition alone it has important consequences for understanding the nature of metal-silicon contacts. This was first conclusively shown for Ti-Si interfaces by Holloway and Sinclair⁽¹⁰⁾. The metal deposits as the room-temperature hexagonal close packed phase. At the metal-semiconductor interface there is an intermediate layer devoid of crystal periodicity (e.g. Fig. 2). This layer is about 2 nm thick and is found whether the silicon is amorphous⁽¹¹⁾ (which is the common form of Si when it is deposited from the vapor phase either by chemical means or by sputtering) or crystalline⁽¹²⁾ and is independent of the substrate doping condition⁽¹³⁾. After a relatively brief annealing treatment (e.g. 30 s at 450°C) significant interdiffusion occurs. The interfacial layer can be more than 10 nm thick at a Ti-Si contact (Fig. 2), and a multilayer stack can be reacted completely by this process⁽¹⁰⁾.

The nature of this reacted layer is shown by high-resolution electron microscopy to be amorphous (Fig. 2). This is confirmed by through-foil electron diffraction of the multilayer specimens⁽¹⁰⁾. Careful radial distribution function analysis of the latter⁽¹⁴⁾ using the method of Moine *et al.*⁽¹⁵⁾ shows that the first nearest neighbor coordination number (between 11 and 12) is typical of an amorphous alloy. At first sight, it is curious that an amorphous material can be produced by reacting together two formerly crystalline phases. However when one considers schematically the free energy-composition diagram for a system in which there is large negative heat of mixing of the constituents (e.g. Fig. 3) it is clear that an amorphous mixture can be thermodynamically favored over the physically separated elements. Of course the compound phases are the most stable and would be produced as equilibrium is approached. Holloway⁽¹⁴⁾ confirmed this model using differential scanning calorimetry. By slowly heating a Ti-Si multilayer sample, two exothermic reactions were observed: the first corresponds to the amorphous phase formation and the second to crystallization at a higher temperature. This phenomenon of "solid-state amorphization" is now well-established for metal-metal systems (e.g. (16)) and is now clearly demonstrated for metal-silicon combinations. Note that because the amorphous alloy has a significantly higher resistivity (about $500 \times 10^{-8} \Omega \cdot \text{m}$ for as-deposited Ti-Si films⁽¹⁷⁾) than that of TiSi₂ or Ti, the electrical contact properties can be modified which has important consequences for their technological application.

In order to assess if this is a more general phenomenon, we investigated other metal-silicon interfaces. The results for Mo-Si multilayers are described by Holloway *et al.*⁽¹⁸⁾. Once again it is clear in the HREM images that an interdiffused amorphous mixture exists at each interface upon deposition alone. Of interest is that the layer is thicker for Mo deposited on Si than vice ver-

Fig. 2 Cross-section high resolution electron micrographs of a titanium thin film on a mono-crystalline silicon substrate: (a) as-deposited, showing a thin (1–2 nm) interdiffused amorphous layer; (b) annealed for 60 s at 400°C for which the amorphous reacted layer has grown to about 10 nm thickness (Ref. (12)).

Fig. 3 A schematic diagram showing free energy versus composition for a typical binary system in which there is negative heat of mixing of the constituents. An amorphous alloy can have lower free energy than of a physical mixture, although the lowest free energy states will occur for the stable compounds in the system. The free energies available for solid-state amorphization (SSAR) and crystallization are indicated.

sa. However upon annealing, crystallization takes place without any extension of the amorphous alloy⁽¹⁸⁾. Similar experiments were carried out on electron-beam evaporated Ni-Si and Co-Si four layer stacks. There is an amorphous mixture at each as deposited metal-amorphous silicon interface⁽¹⁹⁾ which extends upon annealing for the former but crystallizes first for the latter. This different behavior is thought to arise from a second factor which is important in the formation of an amorphous material by solid state reaction⁽¹⁶⁾, namely kinetics. Rapid diffusion of one species into the other strongly promotes this type of reaction, which is indeed the case for the Ti-Si and Ni-Si combinations⁽¹⁹⁾. Reports of an amorphous phase at Rh-Si⁽²⁰⁾, V-Si⁽²¹⁾ and Pt-Si⁽²²⁾ interfaces indicate that the occurrence of an amorphous intermixture must be quite common for silicon-metal interfaces, at least for silicide-forming elements. Indications of metastable phase formation in Al-Si and Au-Si diffusion couples⁽²³⁾⁽²⁴⁾ and HREM photographs of an amorphous layer at an as-deposited Al-Si interface⁽²⁵⁾ further shows that contact structure can be more complex than might first be appreciated.

To summarize, the first step in understanding metal-silicon reactions is by examination of the equilibrium phase diagram. However it is clearly well-established from the above results that an amorphous metastable interfacial layer exists in the majority of cases for as-deposited thin films. If the kinetics of crystallization are sufficiently sluggish, the amorphous phase can grow upon interdiffusion and reaction when it is thermodynamically favored over the separate elements. This behavior needs to be taken into account in any model or interpretation of the electrical contact properties. Fundamental metallurgical principles such as free energy-composition diagrams are useful in explaining the observations and a metastable phase diagram can be derived⁽¹⁴⁾ which shows the composition range over which amor-

phous phase formation can take place.

2. Ternary systems

The proper framework in initiating considerations of ternary systems (i.e. those that involve three elements) is to invoke the use of ternary phase diagrams. Typical situations which arise in microelectronics fabrication include an alloy in contact with silicon, an elemental metal on an insulating silicon oxide or silicon nitride layer, or an elemental metal deposited onto a compound semiconductor. We have shown in several articles (*e.g.* (26)–(28)) that the products of thin film reactions can be correctly predicted in almost all cases using the phase diagram procedure, and this approach is now gaining more widespread acceptance (*e.g.* (29)).

The Gibbs phase rule shows that at constant, arbitrary temperature and pressure a maximum of three phases can exist at equilibrium for ternary systems. In an isothermal section of the phase diagram, an equilateral “composition” triangle is divided into the appropriate regimes of three phase equilibria. The “tie-lines” which bound these regions also connect the two phases which are in mutual equilibrium: i.e. two phases joined by a tie-line are automatically stable in contact with each other. Thus a thin-film deposition of one such phase onto the other will result in no subsequent reaction, so long as the phase compositions are correct.

An example illustrating the power of the phase diagram method is given in Fig. 4. Isothermal sections of the Ti-Si-O and Ti-Si-N diagrams are shown. Of interest is the product of the oxidation or nitridation of titanium disilicide films on a silicon substrate. So long as the temperature is sufficiently high for rapid silicon mobility, the relevant composition region will be close to the silicon corner of the diagram. It is then predicted that SiO₂ will be produced as the third phase in the former case, and TiN in the latter. The importance for processing is that an *insulating* layer (SiO₂) is created by oxidation but that a *conducting* film (TiN) forms during nitridation. Consequently nitridation cannot be substituted for oxidation if a dielectric coating is required for the silicide. Conversely nitridation of TiSi₂ is acceptable in a metallization scheme whereby low resistivity contacts are to be achieved. The titanium nitride in this instance can be employed as an electrically conducting diffusion barrier separating two metal layers (*e.g.* Al and TiSi₂) which might otherwise react during processing.

Phase diagrams of importance to semiconductor manufacture, such as those in Fig. 4, are generally not available in the literature. The conventional means of derivation, heating a large number of compositions to equilibrium in an inert environment followed by phase analysis, is extremely time-consuming. Accordingly we have developed a procedure for calculating the diagrams⁽²⁶⁾ using the tabulated free energies of formation of the phases in the system, noting that a consequence of the Gibbs phase rule is that tie-lines cannot cross one another (since at the point of intersection, four phases

Fig. 4 Calculated ternary phase diagrams in the temperature range 700–1000°C for (a) Ti–Si–O; (b) Ti–Si–N. The tie-line between TiN and Si in the latter indicates that silicon nitride is not a stable product phase for nitridation of a thin titanium disilicide film on a silicon substrate.

would coexist which is not possible for an arbitrary temperature). A computer program has been written which performs the calculations to establish which tie-lines are present⁽³⁰⁾. In our work we employ electron microscopy as a means of determining whether thin films in contact react during heating, with any reaction products identified by high-resolution imaging, microdiffraction or microchemical analysis. Only a thin reacted layer (*e.g.* less than 5 nm) in a cross-section sample is often sufficient for proper work.

It is worthwhile mentioning that metal contacts to gallium arsenide and other compound semiconductors represent an important example covered by ternary phase diagrams. Most elemental metals are not in thermodynamic equilibrium with GaAs (*i.e.* a tie-line does not connect the metal phase with the semiconductor), the most common type of diagram being that illustrated schematically in Fig. 5⁽³¹⁾. In such a case heating the metal film on a GaAs substrate results in the formation of two new phases, in Fig. 5 those being a metal gallide and a metal arsenide phase. Because arsenic has relatively low atomic mobility in such circumstances, the arsenide often forms a continuous film in contact with the GaAs with the intermetallic metal gallide on top (*e.g.* (32)–(34)). This can increase the Schottky barrier height (*e.g.* (33)) even when only a few nanometers of interfacial reaction

Fig. 5 The most common metal (M)-gallium-arsenic ternary phase diagram, the tie-lines of which indicate that the elemental metal is not thermodynamically stable in contact with a GaAs substrate. This is the type IV diagram in the scheme of Beyers *et al.*⁽³¹⁾.

have taken place. Accordingly the issue of phase stability, and the application of phase diagrams, is important in the proper choice of metal contacts to GaAs.

Moreover, it can be appreciated that the diagrams can be used to predict phases which would already be stable in contact with the semiconductor and thus cause minimal disruption to the interface upon annealing⁽³¹⁾. Such is the case for Si on GaAs (and of course vice versa), Au₂Ga⁽³⁵⁾ or CoGa⁽³⁶⁾ on GaAs. However, as with the silicon-based systems the majority of relevant phase diagrams do not exist experimentally and are only now being derived (*e.g.* (37)). Their calculation is more problematic because of the scarcity of thermochemical data for reactions involving gallium or arsenic, although several diagrams can be deduced from the products of thin film reactions⁽³¹⁾. There remains an immense amount of work to be carried out to achieve a satisfactory level of information, not only for GaAs but for the other compound semiconductors as well (*e.g.* InSb, CdTe, etc.).

3. Quaternary systems

Because of the complexity of modern semiconductor processing, it is apparent that even ternary diagrams are an insufficient source of knowledge. For alloys in contact with dielectric SiO₂ or Si₃N₄ (and even silicon oxynitride), alloy or compound diffusion barriers separating Al from Si, alloy contacts to compound semiconductors, or one compound semiconductor grown on another, four or more elements can coexist at a particular interface. Specific examples include Ti–Si–O–N (for titanium on silicon oxynitride), Ti–W–Al–N (for (TiW)N diffusion barrier with Al), Au–Ge–Ni–Ga–As (for the classic ohmic contact to gallium arsenide) and many others. In such cases understanding phase stability involves the use of quaternary and higher order phase equilibria. Since the number of phases mutually stable at equilibrium is increasing, then so does the complexity of the situation. A systematic framework employing the phase diagram method is therefore even more pressing.

We have initiated an effort in deriving such diagrams, as an extension of our approach for ternary systems⁽³⁰⁾. As before, traditional phase diagram determinations are out-of-the-question. Instead we calculate the diagrams

Fig. 6 The calculated Ti-Si-O-N quaternary phase diagram in the temperature range 700–1000°C. The heavy, dashed lines are the interior (quaternary) tie-lines, which show that TiN is a particularly “dominant” phase in this system, being stable in contact with TiSi_2 , SiO_2 , Si_3N_4 , TiO , etc. (Ref. (30)).

using established, or reasonably estimated⁽³⁰⁾, values for the free energy of formation of the compounds in the system. By testing all possible “competing” tie-lines against one another, and tie-lines (i.e. two-phase equilibria) against possible tie-planes (i.e. three-phase equilibria) it is possible to establish the tie-line distribution in the diagram. Since a fourth element is involved a regular tetrahedron is a convenient way to display the data, although some degree of scrutiny is required to deduce the pertinent information.

Figure 6 shows an example for the Ti-Si-O-N system. The faces of the tetrahedron represent the four component ternaries (two of which were already described in Fig. 4). However the interior (quaternary) tie-lines are quite crucial since these demonstrate the phases to be mutually stable when all four elements are involved at an interface. For instance from Fig. 6 it can be concluded that TiN is stable with SiO_2 , and so that a titanium nitride film would not decompose a dielectric silicon oxide layer upon heating. Conversely Ti itself is not stable with any of the dielectrics e.g. SiO_2 , Si_3N_4 or silicon oxynitride. In fact it can be predicted that heating a Ti thin film on the latter would first give rise to TiO , Ti_5Si_3 and TiN as product phases and this has been confirmed by Auger spectroscopy and electron microscopy⁽³⁸⁾.

For compound semiconductors, such diagrams can be used to identify stable depositions. Because of their large free energy of formation, metal aluminides are likely to be stable phases when combined with III-V semiconductors and we suggest that the possible quaternary diagram for the Ni-Al-Ga-As system is that shown in Fig. 7. The tie-line between NiAl and GaAs is consistent with the experimental observation by Sands⁽³⁹⁾ that NiAl can be annealed without reaction on GaAs at 600°C. The complete diagram still requires further work, largely (as mentioned earlier) because of the paucity of thermochemical data for some of the compound phases. In a related vein,

Fig. 7 The suggested Ni-Al-Ga-As quaternary phase diagram at room temperature indicating that NiAl is a stable phase in contact with the compound semiconductor GaAs. This diagram was calculated using known thermochemical data for the majority of the compounds, with those for the remainder (i.e. the Ni-Ga phases) estimated using the method of Miedema *et al.*⁽⁴²⁾. Accordingly it should be regarded as highly tentative at present, with some tie-lines omitted completely since they are so uncertain.

Schwartzman has shown that various II-VI compounds (e.g. CdTe, ZnTe) are chemically stable on GaAs substrates, both by calculation and experimentation, and that extremely distinct interfaces are obtained upon annealing, quite unlike those such as in Fig. 2 in which interfacial reaction takes place.

4. *In situ* HREM of interface reactions

The study of reactions at metal-semiconductor interfaces can follow conventional procedures, of heating the sample in an inert environment followed by sectioning for TEM analysis. It is also possible to carry out the heating in the TEM itself and to follow the reaction *in situ* as it occurs. The major question then arises as to whether the same behavior takes place as that in the bulk sample. This can be decided by comparing the result of the reaction in both situations. For Ti-Si and Mo-Si multilayers, we find that there are exactly equivalent reaction sequences. Firstly in Ti-Si, the amorphous phase growth occurs in a planar manner in both experiments⁽¹¹⁾ and Kirkendall voids are produced in the place of the consumed silicon since this is the dominant diffusing species. This latter observation alone indicates that bulk diffusion is taking place and in fact it is a remarkable demonstration of the Kirkendall effect, well-known in the metallurgical field. In the Mo-Si system, crystallization precedes interdiffusion and no Kirkendall voids are formed in either heat treatment⁽¹⁸⁾. The fact that an interfacial reaction is similar in TEM thin foils to that in bulk is perhaps not so surprising since atomic interactions involving only a few atomic replacements are necessary. When microstructural observations are combined with

kinetic measurements and determination of the activation energy (*e.g.* (40)) one can be quite certain that similar processes are being followed.

Our work introducing *in situ* HREM has recently been reviewed⁽⁴¹⁾. Besides the reactions described above, we have also applied the method to investigate solid phase epitaxial regrowth of silicon, some metal-gallium arsenide reactions and the stability to annealing of the GaAs–CdTe interface. To-date only the GaAs studies have proved to be problematic: if the reaction releases metallic gallium before the latter can be incorporated into a gallide intermetallic compound then the thin film experiment can differ from that of the bulk. Otherwise, all the advantages of *in situ* observations can be obtained, but at a resolution capable of imaging atomic behavior directly. This provides us with the possibility of more rapidly assessing the chemical behavior of a metal-semiconductor interface, in one observation period, compared to a series of conventional, cross-section bulk samples. In our very latest studies we have been successful in recording the nucleation and growth of silicon crystallites in amorphous silicon in a nominal temperature range of 700–775°C, and this will be reported in due course. Clearly these experiments significantly expand the application of high resolution microscopy in studying silicidation and other interesting reactions.

IV. Summary

Electron microscopy, especially at high-resolution, is extremely valuable in studying reactions and stability at metal-silicon and other semiconductor interfaces. However interpretation of reaction behavior requires an appropriate framework based on sound thermodynamic principles. Phase diagrams provide such an approach. As the number of elements involved at an interface increases, then so does the complexity of the system, requiring higher-order phase equilibria. Most pertinent diagrams are not available in the literature but can be calculated using the methods we describe. The possibility of metastable product phases, even amorphous in nature, must also be borne in mind. But, the combination of the scientific understanding of interfacial reactions together with careful, detailed microstructural analysis by electron microscopy is becoming increasingly important in developing reliable microelectronic circuits.

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