Application of equilibrium thermodynamics to the development of diffusion barriers for copper metallization

(Invited)

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Abstract

The guidelines for designing a conductive, amorphous material, capable of thermodynamic equilibrium with copper, are defined using readily available thermodynamic information. The tradeoff between desired properties — equilibrium at the interfaces, amorphous microstructure, and electronic conductivity — are described, along with trends in relevant binary systems that result in these properties. These guidelines maximize the thermodynamic tendency for amorphous phase formation, in an attempt to minimize the need for nonequilibrium synthesis methods. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

An implicit requirement for continuously decreasing device sizes is the increased performance of the materials from which these devices are fabricated. Technology has reached the level at which materials properties (e.g., microstructure, dielectric function, etch rate) become design parameters.

As described in a review article by Wang [1], the transition from aluminum to copper metallization exemplifies the need for robust materials design, in that the required properties of Cu-compatible diffusion barriers are in conflict. In addition to these solid-state materials requirements, fabrication method also becomes a critical issue. Physical vapor deposition (PVD) has been used to successfully make amorphous, conductive diffusion barriers for Cu metallization [2–4], but with increasing device aspect ratios and trench depths, these line-of-sight deposition techniques are inadequate. Chemical vapor deposition (CVD) techniques can uniformly coat high aspect ratio devices, but tend to produce crystalline phases of metallic materials. Thus, CVD of amorphous, conductive, diffusion barriers requires systems with the strongest thermodynamic propensity for amorphization.

Although these materials also need to prevent diffusion into the dielectric layers, we have chosen to analyze a hypothetical stack consisting of Si/barrier/Cu. There are currently a variety of options for

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low-\(k\) dielectrics, none of which have been described using thermodynamic data. Additionally, compatibility with both Si and Cu is a more rigorous thermochemical requirement.

There are three main requirements for an ideal diffusion barrier. First, the material should be electronically conductive [2], with a resistivity less than 1 m\(\Omega\) cm. Second, the material should not react with any of the other materials (Cu, Si or dielectric). Finally, since grain boundary diffusion is typically rapid in these materials, an ideal barrier should have an amorphous microstructure.

These requirements are typically in conflict with each other — finding a material (that is conductive and amorphous and nonreactive) is difficult. As discussed below, stabilization of an amorphous microstructure typically requires several elements in the system, plus a certain amount of directional bond character. As more elements are incorporated into the system, the chemical potentials (the thermodynamic description of each element’s reactivity) of the other elements change, and the requirement of interfacial stability is often lost. As bond character becomes more directional (indeed, covalent), the solid tends to form a band gap, and electronic conductivity is lost.

Section 2 describes the use of thermodynamic calculations to define the conditions of nonreactivity at the interfaces. Specifically, for each element that goes into the diffusion barrier, what are the concentration limits within which we predict equilibrium at the interfaces? After discussing the interfacial stability requirement, Section 4 defines the equilibrium thermodynamic conditions that can result in a stable amorphous phase. Although amorphous phases are non-equilibrium, their presence can often be predicted by equilibrium thermodynamic properties. Systems with tendencies toward amorphization can be separated from those that tend toward crystallinity. The goal of the thermodynamic calculations is to maximize the tendency for amorphous phase formation with the minimum number of elements.

### 2. Interfacial stability

One of the main thermochemical differences between aluminum and copper metallization is shown by their reactivities with silicon: Al and Si can exist in equilibrium, Cu and Si form Cu–silicides. Thus, pure Cu and pure Si cannot exist together at equilibrium. This nonequilibrium results in more stringent criteria for the diffusion barrier: the thermodynamic driving force for diffusion is greater in Cu/Si vs. Al/Si, and far fewer materials are compatible at the interfaces of the Cu/Si system.

Consider a hypothetical Co–Si-based layer between Si and Cu: (1) CoSi\(_2\) is in equilibrium with silicon, but is expected to react with copper under standard state conditions:

\[
\text{CoSi}_2 + 3\text{Cu} \Rightarrow \text{Cu}_3\text{Si} + \text{CoSi}
\]  

(2) Co\(_2\)Si is in equilibrium with Cu, but is expected to react with silicon under standard state conditions:

\[
\text{Co}_2\text{Si} + \text{Si} \Rightarrow 2\text{CoSi}
\]  

Using established thermodynamic data and minimization software [4–6], our calculations show that, in general, silicides of the form TMSi\(_2\) (TM, transition metal) are reduced by copper to form Cu\(_3\)Si. Lower silicides (e.g., TM\(_3\)Si\(_2\)) which can be in equilibrium with copper, are not in equilibrium with silicon.
Table 1
Potential components of diffusion barrier, grouped by bond pair

<table>
<thead>
<tr>
<th>Binary system</th>
<th>Solid solubilities</th>
<th>Crystal structures</th>
<th>Amorphization tendency</th>
<th>Electrical conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM–N</td>
<td>Broad</td>
<td>Simple</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>TM–Si</td>
<td>Narrow</td>
<td>Simple</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>TM–B</td>
<td>Narrow</td>
<td>Simple</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Si–N,B–N</td>
<td>Narrow</td>
<td>Simple</td>
<td>Poor</td>
<td>Good</td>
</tr>
</tbody>
</table>

The diffusion barrier will possibly be composed of at least one transition metal, plus a metalloid such as Si or B, and N. Table 1 divides these elements into bond pairs: TM–N, TM–metalloid, and metalloid–N. While the effects of each bond type are discussed later, one can see that a combination of these elements, plus the Si and Cu interfaces, leads to a complex system of equilibria.

Many of the effects of the various components, different transition metals, Si, N, and B, can be shown using binary phase diagrams. Figs. 1–4 show simplified versions of the Cu–TM, TM–Si,
Fig. 2. Simplified binary silicide phase diagrams; liquid phases (hence eutectics) have been omitted for clarity. Left side of each diagram is pure metal, right side is Si. Intermetallic phases are shown by their compositions and melting points (°C).

TM–B, and TM–N binary phase diagrams. To show important trends, the diagrams are arranged according to the position of each element in the periodic table. Because we are concerned with solid state properties, liquid phases have been omitted for clarity. The intermetallic phases are shown by their compositions and melting points [7].

Fig. 1 shows relevant TM–Cu binary phase diagrams, and demonstrates the difference between transition metals from groups (III and IV) vs. (V and VI). Group IV transition metals (e.g., Ti) form stable cuprides, as does silicon. Group V and VI transition metals, as well as B, are stable with Cu. This difference yields the first criteria for equilibrium at the Cu interface: The chemical potentials of the group III and IV transition metals in the diffusion barrier layer must be kept low, and the chemical potential of silicon must be kept low. This maximum chemical potential for each element is given by the two phase equilibrium between Cu and the most copper rich TM–cupride.

Fig. 2 shows the simplified TM–silicon binary phase diagrams. Note that nearly all metals form several stable silicides. This strong TM–Si bonding shows that changing the silicon concentration in the diffusion barrier will change the chemical potentials of all other components in the barrier. Conversely, changing any other component’s concentration will change the chemical potential of silicon, which can react with Cu. For thermodynamic equilibrium, only the most silicon-rich silicide is in equilibrium with Si.

Fig. 3 shows the TM–boron binary phase diagrams. As with silicon, boron forms stable compounds
Fig. 3. Simplified binary boride phase diagrams; liquid phases (hence eutectics) have been omitted for clarity. Left side of each diagram is pure metal, right side is B. Intermetallic phases are shown by their compositions and melting points (°C).

Fig. 4 shows the TM–nitrogen binaries. Note the instability of Mo and W nitrides, compared to other TM nitrides and Si$_3$N$_4$. We have found that Mo and W nitrides can form relatively easily during CVD processes, although they are thermodynamically unstable. Cu–nitrides are similar: they have been observed experimentally, but their thermodynamic stability is not well characterized. Because the nitrides of Cu, W and Mo appear to be of similar stabilities, we expect differences between the interfaces of (Cu–Mo$_2$N or Cu–W$_2$N) and (Cu–TiN, Cu–TaN, etc.). While we expect nonreactivity at (for example) the interface between TaN and Cu, we do not necessarily expect nonreactivity at the interface between Mo$_2$N and Cu or W$_2$N and Cu.

Another result of the instabilities of the W/Mo–nitrides is the dominance of Si$_3$N$_4$ in the ternary systems. While Section 4 details the results of this dominance, the following section introduces the use of ternary phase diagrams to describe these systems.

3. Simplified ternary phase diagrams

The effect of changing nitride stability on phase assemblage is most easily shown with a ternary phase diagram. These diagrams show the stable phases present at constant temperature (in this paper,
Fig. 4. Simplified binary nitride phase diagrams; liquid phases (hence eutectics) have been omitted for clarity. Left side of each diagram is pure metal, right side is N. Intermetallic phases are shown by their compositions and melting points (°C). The nitrides of Mo and W are generally unstable at 1 atm nitrogen pressure, but tend to form easily during CVD processes.

625°C), and a pressure of 1 atm, for a system of three components. The ternary diagrams shown here do not consider solution phases and ternary phases, and are thus approximations. However, in that the thermodynamic data for the binary compounds have been well assessed [4,5], these diagrams can accurately compare the stabilities of different binary compounds. Fig. 5 compares two ternary systems, Ta–Si–N and Mo–Si–N. Both systems contain very stable TM–silicides, but nitrides of very different stabilities: Mo$_2$N is unstable at 1 atm, TaN and Ta$_2$N are very stable. As a result, Si$_3$N$_4$ is present at all compositions in the MoSiN system, whereas the Ta-rich corner of the TaSiN system contains Ta–nitrides and Ta–silicides, but not Si$_3$N$_4$. As discussed in Section 4, increased Si$_3$N$_4$ phase content increases amorphizability, but reduces electrical conductivity significantly. Thus, the choice of transition metal (e.g., Ta vs. Mo) is expected to have a large effect on Si$_3$N$_4$ phase stability, and hence electronic conductivity.

Ternary phase diagrams have also been used to show the stability ranges of different silicides with copper [8]; this analysis can be extended to TM–N–Cu systems. Fig. 6 compares the Ta–Cu–N and Ti–Cu–N phase diagrams, and shows the effect of choosing a Group V/VI vs. Group IV transition
metal on stability vs. Cu. The lack of Ta–Cu compounds yields a broad range of compositions in equilibrium with Cu. For the Ti system, compositions more Ti-rich than Ti$_2$N are expected to react with Cu.

The interfacial stability challenges are summarized in Fig. 7, which schematically shows the maximum chemical potentials at each interface (Si and Cu), beyond which we expect reaction. There are no species for which a high chemical potential can be supported at both interfaces: this is the inherent reactivity challenge. There are two separate solutions: keep all chemical potentials low, or relax the requirement for reactivity at the silicon interface.

These two solutions are not exclusive. For any phase composed of multiple elements, the more stable the phase, the lower the relative chemical potential of the elements within the phase, relative to
Fig. 7. Required chemical potentials at each interface for stability. Silicon interface (left side) cannot tolerate high chemical potentials of any other species. Copper interface (right side) can tolerate high chemical potentials of N, B, group V, and group VI transition metals. Chemical potential of Si and group IV transition metals must be kept low at Cu interface.

their pure states. Thus, compounds with high melting points tend to be less reactive than compounds with lower melting points. This result suggests the use of TM–boride phases. Our calculations predict equilibrium between TiB<sub>2</sub> and Cu, and between TiB<sub>2</sub> and Si, in agreement with prior experimental work [9]. Of the electronically conductive materials with tendency toward amorphous phase formation, TM–diborides were the only materials found to be in equilibrium with both Si and Cu.

The relaxation of equilibrium with Si may also be a realistic assumption. Our calculations do not show equilibrium between TiN and Si. This system is predicted to decompose to TiSi<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, which has been observed experimentally [10]. However, TiN films on Si have been used extensively in microelectronics, due to kinetic constraints on equilibrium. Multivalent metals such as Cu are highly catalytic, and previous work has shown the reactivity of Cu at temperatures as low as 250°C [11–13], Thus, we require thermodynamic equilibrium with copper, but can perhaps relax the requirement of equilibrium with silicon.

Ternary thermodynamic calculations show that silicides based on group IV metals are generally stable with Cu only near 50:50 compositions (e.g., TiSi). Group V and VI compounds have a much broader range of compositions in equilibrium with Cu; in general, silicides that are more metal-rich than MeSi<sub>2</sub> are stable with Cu. For nitrides, all Group V nitrides are stable with Cu, while for group IV nitrides (e.g., TiN), only 50:50 compositions are stable with Cu. The nitrides of W and Mo are relatively unstable, as are those of Cu, but the relative stability of (W or Mo) nitrides vs. Cu–nitrides has not been determined.

4. Amorphization

Efforts to synthesize amorphous metals have been reported since 1934 [14–16]. Although the envisioned usage of these materials has been in bulk magnetic applications, we attempt to apply results from this research to our search for amorphous, conductive diffusion barriers.
The synthesis of conductive, amorphous metals by quenching from liquid began in the 1960s [17]. Very fast cooling techniques ($1E^6$ K/s) created a variety of metallic glasses, but these materials were generally unstable. A ‘second generation’ of metallic glass synthesis began with work in the early 1990s [18]. These materials focused on compositions that were thermodynamically more stable, and thus formed glasses at much slower cooling rates ($1E^{-1}$ K/s). Table 2 compares the salient issues of these two methods of glass formation, showing the challenges with using CVD to make amorphous, conductive films.

The thermodynamic prerequisites for amorphous metal stability are continuously being defined and debated [19–21] but can be broadly summarized:

The energy of the amorphous phase should be as close as possible (i.e., not much greater) than the energy of the competing stable phases.

A certain degree of directional bonding (in the limits, covalency) is needed. SiO$_2$ forms amorphous phases easily, face centered cubic metals do not.

Metals with similar electronic structure but different sizes should be chosen. This result suggests mixing different transition metals.

Compositions should be chosen so that several crystalline phases are stable. This requirement suggests finding a two-phase region of a binary system, a three-phase region of a ternary system, etc.

The competing stable phases should have very different compositions, complex crystal structures, and no tolerance for solid solubility. From a thermodynamic standpoint, we seek compositions in which the number of solid phases equals the number of components in the system. These multi-phase regions should be large: as wide as possible on a binary phase diagram, largest surface area for an isothermal ternary diagram, largest volume for a quaternary phase diagram, etc.

The objective of these requirements is to frustrate the formation of crystalline phases. By choosing a phase region with very different compositions, and crystal structures which are intolerant of stoichiometric deviation, the probability that a random adatom on a given crystalline nucleus will be

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Pathways to synthesize amorphous solids</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetics</strong></td>
<td><strong>Thermodynamics</strong></td>
</tr>
<tr>
<td>Quench rapidly from disordered (liquid, gas) state</td>
<td>$\rightarrow$–How $\rightarrow$</td>
</tr>
<tr>
<td>Nondirectional (metallic) Conductive</td>
<td>$\rightarrow$–Bonding $\rightarrow$</td>
</tr>
<tr>
<td>Fast ($1E^6$ K/s)</td>
<td>$\rightarrow$–Conductivity $\rightarrow$</td>
</tr>
<tr>
<td>Aluminum cannot quench to amorph.</td>
<td>$\rightarrow$–Minimum cooling rate to yield amorphous phase $\rightarrow$</td>
</tr>
<tr>
<td>Less stable</td>
<td>$\rightarrow$–Stability $\rightarrow$</td>
</tr>
<tr>
<td>PVD</td>
<td>$\rightarrow$–Thin film techniques $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td>Energy of amorphous phase similar to energy of competing crystalline phases</td>
</tr>
<tr>
<td></td>
<td>Directional (covalent)</td>
</tr>
<tr>
<td></td>
<td>Insulating</td>
</tr>
<tr>
<td></td>
<td>Slow ($1E^{-1}$ K/s)</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$ Cannot quench to crystalline</td>
</tr>
<tr>
<td></td>
<td>More stable</td>
</tr>
<tr>
<td></td>
<td>CVD</td>
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</tbody>
</table>
suitable for growth of the crystal decreases. Growth of the nuclei then requires diffusion, which we hope to minimize. Table 1 generalizes the tendency of the different barrier materials to fulfill these requirements.

A direct result of these requirements is the exclusion of the Group IV TM–nitride phases. As shown in Fig. 4 and Table 1, these nitrides have broad ranges of solid solubility, and simple crystal structures. As a result, these structures are ‘flexible’ to deviations from stoichiometry which can occur during crystal growth. The crystal structure accommodates defects (strain) during crystal growth, so crystalline phase formation is not suppressed.

The instability of the Mo–N and W–N phases suggests that these materials might form amorphous phases easily. Because the difference in stability between competing amorphous and crystalline phases is important, unstable crystalline phases can enhance amorphous phase formation.

TM–silicides have some directional bonding, resulting in more complex crystal structures with limited tolerance for solid solubility. Thus, we expect these materials to form amorphous phases if kinetic ‘helpers’ are used: low deposition temperatures, plasma, etc. [22,23]. TM–borides have fairly complex crystal structures, with little tolerance for solubility. We expect these materials to form amorphous phases fairly easily [11,24].

Combining several of these binary systems (e.g., TM–Si and TM–N) can increase the number of competing stable phases, and thus increase amorphization tendency. However, reaction between the nonmetal constituents (Si, B, N) is also important. Si₃N₄ is stable and highly covalent, and amorphous Si₃N₄ is easily made using CVD. However, Si₃N₄ is an insulator, so percolation effects are expected; increasing Si₃N₄ phase content increases both amorphization tendency and resistivity.

These effects agree with previous experimental work on TM–Si–N based diffusion barriers [2,3,8,25,26] which show that single-phase films with compositions in the Si₃N₄ phase field have both strong tendencies for amorphization and poor electronic conductivity. A critical question is whether the Si₃N₄ phase field is a requirement for amorphous phase stabilization.

5. Compromise and conclusions

As shown in the previous sections, the thermodynamic requirements for interfacial stability, amorphization, and conductivity are conflicting. Amorphization requires many elements, but this increases the possibility of reaction at the interfaces. For a ternary system, a broad three-phase region (for amorphization) also requires that all three phases be stable with copper. For group IV TM–nitrides and TM–silicides, only regions of the binaries near 50:50 compositions are stable with copper. Group VI silicides are very stable, but group VI nitrides are unstable. Thus, for ternary TM–N–Si systems, (Mo/W)–N–Si compositions are always expected to contain Si₃N₄, whereas TM-rich compositions in the Group IV–N–Si and Group V–N–Si systems are expected to contain silicides and nitrides, without Si₃N₄.

The thermodynamic modeling techniques suggest two areas for future work. Because TM–diborides are predicted to be stable with both Cu and Si, diboride mixtures are expected to satisfy the diffusion barrier requirements. Following the topological requirements suggesting a maximum size mismatch, mixtures of TM–diborides should be chosen with differently sized transition metals. The advantage of a ternary TM–TM–B system is that nitrogen might not be necessary for amorphous phase formation. Thus, insulating phases (BN) can be avoided, there are fewer elements to react with Cu, and processing does not require a nitrogen source.
For TM–N–Si systems, the critical question seems to be Si₃N₄ phase stability. It has been well established that films with global compositions in regions where Si₃N₄ is stable tend to form amorphous phases easily. [2,3,24–26] However, amorphous phase formation in regimes where Si₃N₄ is not stable is an interesting challenge. These compounds may require additional elements, such as multiple transition metals, to frustrate crystallization. A mixture of groups V and VI transition metals could provide the necessary phase assemblage. Consider the Mo–Ta–Si–N system: both Ta–silicides and Mo–silicides are very stable, as are Ta–nitrides. However, Mo–nitrides are unstable. Compositions in the three-phase region of the Mo–Ta–Si ternary containing Mo₃Si, Ta₃Si, and Mo₃Si₃ are all expected to be in equilibrium with Cu. Due to the difference in stability of the TM–nitrides, nitrogen addition to this phase regime is predicted to form TaN, rather than Si₃N₄. Thus, the predicted phase composition of the system — TaN, Mo₃Si, Ta₃Si, and Mo₃Si₃ — consists of four conductive phases, each in equilibrium with Cu.

These systems are perhaps technologically unfeasible. The objective of this paper is to show how relevant technological issues — reactivity, microstructure — can be classified using simple thermodynamic information. These simple modeling techniques can exclude many systems from experimental study. More thorough analyses of quaternary systems can predict specific regions of specific systems where desired properties may be found.

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References