Thermal stability of the interfaces between Co-, Ni-, and Fe-based ferromagnets in contact with selected nitrides $MN$ ($M=\text{Al}, \text{B}, \text{Nb}, \text{Ta}, \text{Ti}, \text{and} \text{V}$)

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Nitride tunnel barriers have potential applications in magnetic tunnel junctions (MTJs). Thermal stability of the interfaces between Co-, Ni-, and Fe-based ferromagnets and these nitride tunnel barriers is critical to device performance. With guidance from low-temperature ternary isothermal phase diagrams of the $\text{Co}–M–\text{N}$, $\text{Ni}–M–\text{N}$, and $\text{Fe}–M–\text{N}$ systems ($M=\text{Al}, \text{B}, \text{Nb}, \text{Ta}, \text{Ti}, \text{and} \text{V}$), the interfaces in $\text{Co}/MN$, $\text{Ni}/MN$, and $\text{Fe}/MN$ structures were evaluated in terms of two criteria: (1) be in equilibrium with each other (i.e., connected by a stable tie line) and (2) have negligible mutual solubility in the phase diagram at the temperatures of interest. Of the investigated interfaces, $\text{Co}/\text{AIN}$, $\text{Co}/\text{BN}$, $\text{Co}/\text{NbN}$, $\text{Co}/\text{TaN}$, $\text{Co}/\text{TiN}$, $\text{Ni}/\text{BN}$, $\text{Ni}/\text{TaN}$, $\text{Fe}/\text{BN}$, $\text{Fe}/\text{NbN}$, $\text{Fe}/\text{TaN}$, and $\text{Fe}/\text{TiN}$ were found to be thermodynamically stable. However, in light of some simplifications made in this analysis, the current evaluation of interfacial stability serves as a useful step in preselecting candidate nitride-based MTJ tunnel barrier materials for detailed study.


INTRODUCTION

Magnetic tunnel junctions (MTJs) consist of two ferromagnetic metallic electrodes separated by an insulating (tunnel barrier) layer and are being investigated for their applications in magnetic random access memories (MRAMs) and tunneling magnetoresistive (TMR) read heads. In order for successful operation in practical devices, MTJs must exhibit favorable characteristics such as uniformity of chemistry and structure of the insulator (tunnel barrier) layer, thermodynamic stability, and smoothness and abruptness of the ferromagnet-insulator interface.$^1$ Some metal oxides, such as $\text{Al}_2\text{O}_3$ and $\text{MgO}$, have been widely used as tunnel barrier materials.$^2–^4$ In a previous study,$^5$ we investigated the thermodynamic stability of $\text{Co}$ in contact with the tunnel barriers of selected oxides based on the widespread use of $\text{Co}$ and $\text{Co–Fe}$ alloys (with $\text{Fe}$ concentrations near 10 at. %) as ferromagnets in TMR devices. Specifically, we investigated isothermal sections of the following systems: $\text{Co}–\text{Al}–\text{O}$, $\text{Co}–\text{Ti}–\text{O}$, $\text{Co}–\text{Mg}–\text{O}$, $\text{Co}–\text{Gd}–\text{O}$, $\text{Co}–\text{La}–\text{O}$, $\text{Co}–\text{Si}–\text{O}$, $\text{Co}–\text{Ta}–\text{O}$, $\text{Co}–\text{Hf}–\text{O}$, $\text{Co}–\text{Zr}–\text{O}$, and $\text{Co}–\text{Y}–\text{O}$. In that study, two principles were applied to identify potential metals to form oxide tunnel barriers. One is that the metal should be a good oxide former. In other words, the metal oxide should have a large negative Gibbs energy of formation. The other is that the insulator barrier should have a low band gap and therefore, lower junction resistance.$^6$ Recent studies showed that some metal nitrides have advantages over metal oxides and could be promising alternate tunnel barrier materials.$^7–^1^2$ For example, $\text{AlN}$ has the following advantages over $\text{Al}_2\text{O}_3$: (1) $\text{AlN}$ can be sputter deposited using a single-step, oxygen-free reactive process in which electrode oxidation can be avoided. (2) Unlike amorphous $\text{Al}_2\text{O}_3$, $\text{AlN}$ is crystalline and may therefore present advantages in terms of growth and surface characteristics. (3) $\text{AlN}$ exhibits higher thermal conductivity and has a high bulk dielectric strength of 60 mV/A. (4) For an $\text{AlN}$ tunnel barrier, the nitrogen content can be varied to possibly manipulate the density and effective barrier height.

In addition to $\text{AlN}$, nitrides such as $\text{BN}$, $\text{Si}_3\text{N}_4$, and $\text{AlON}$ have also been used as tunnel barriers. Table I lists published data on TMR and junction resistances from these barriers. These studies stimulate research interest in nitrides as potential tunnel barrier materials. The present study will use a similar, but more sophisticated [CALPHAD (Ref. 13)] approach than that used for identifying oxide tunnel barriers to select stable nitride tunnel barriers. In other words, we evaluate the thermodynamic stability between selected nitride tunnel barriers and ferromagnetic layers such as $\text{Co}$, $\text{Fe}$, and $\text{Ni}$ to identify candidate nitride barriers. The remainder

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of this article begins with the discussion on the selection of metals to form potential metal nitrides, and then the calculation of low-temperature isothermal ternary phase diagrams, and finally the conclusions about thermodynamic stability based on these calculations. A similar analysis procedure was used by Schloam and Haeni in their search for stable gate dielectrics in contact with Si.

**METAL SELECTION AND CALCULATION METHOD**

The metals chosen for study were selected based on the same two principles used in the oxide study, except now we concentrate on good nitride formers. The enthalpies of formation and band-gap energies (when available) of the corresponding metal nitrides are listed in Table II. In addition to these six candidate materials, some other elements also form very stable nitrides, such as Hf, Y, Zr, and La, but were not evaluated in this study due to lack of binary thermodynamic descriptions. Table II provides some insight into why nitride barrier materials to form potential metal nitrides, and then the calculation of low-temperature isothermal ternary phase diagrams, and finally the conclusions about thermodynamic stability based on these calculations. A similar analysis procedure was used by Schloam and Haeni in their search for stable gate dielectrics in contact with Si.

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**TABLE II. Comparisons between enthalpies of formation, band-gap energies, and crystal structure of investigated nitrides and Al2O3.**

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Enthalpy of formation (kJ/mol atoms)</th>
<th>Band-gap energy (eV)</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIN</td>
<td>−159</td>
<td>6.02 (semi)</td>
<td>hP4</td>
</tr>
<tr>
<td>BN</td>
<td>−126</td>
<td>4.6</td>
<td>cF8</td>
</tr>
<tr>
<td>TiN</td>
<td>−169</td>
<td>3.35–3.45</td>
<td>cF8</td>
</tr>
<tr>
<td>VN</td>
<td>−109</td>
<td>N/A</td>
<td>cF8</td>
</tr>
<tr>
<td>NbN</td>
<td>−118</td>
<td>N/A</td>
<td>cF8</td>
</tr>
<tr>
<td>TaN</td>
<td>−180</td>
<td>Ta2N; 2.1</td>
<td>hP6</td>
</tr>
<tr>
<td>Al2O3 (corundum)</td>
<td>−335</td>
<td>9</td>
<td>hR30</td>
</tr>
<tr>
<td>Co2N</td>
<td>2</td>
<td>N/A</td>
<td>oP6</td>
</tr>
<tr>
<td>FeN</td>
<td>N/A</td>
<td>N/A</td>
<td>cF8</td>
</tr>
<tr>
<td>Fe2N</td>
<td>−16</td>
<td>N/A</td>
<td>hP2</td>
</tr>
<tr>
<td>FeN</td>
<td>−17</td>
<td>N/A</td>
<td>cP5</td>
</tr>
<tr>
<td>Ni2N</td>
<td>0.2</td>
<td>N/A</td>
<td>hP8</td>
</tr>
</tbody>
</table>

The CALPHAD method, a well-established approach for calculating phase diagrams and thermodynamic properties, was used to calculate the isothermal ternary phase diagrams of the (Co, Ni, or Fe)–M–N systems. The heart of the CALPHAD approach is the Gibbs energy function modeling of a phase. A unique feature of this approach is that the excess Gibbs energy of a phase in a higher system can be extrapolated from those of the same phases in the lower-order systems, through which the phase equilibria in a higher-order system can be calculated. In the following, the Fe–Ti–N will be used as an example to show how the Gibbs energy function of a ternary phase can be extrapolated from the lower-order systems. If this ternary system is considered as a higher-order system, the lower-order systems of interest are three binary systems: Fe–Ti, Ti–N, and Fe–N. Three categories of phases exist in these three binaries: disordered solution phases and compound phases with and without homogeneity ranges. For example, the Fe solid solution phase based on the bcc structure belongs to the category of disordered solution phases, while Fe2N and FeN are compound phases with and without homogeneity ranges, respectively. The Gibbs energy function for each phase in these three binaries was well modeled in terms of extensive experimental data and they were directly applied to extrapolate the Gibbs energy function of the phase in the Fe–Ti–N ternary system. Several methods exist to determine the extrapolation formula. Hillert analyzed various extrapolation methods and recommended the use of the method of Muggianu et al.

The Gibbs energy of a ternary solution phase such as bcc can be determined by extrapolation of the binary energies using the method of Muggianu et al., which is given by

\[
G^{bcc} = x_Fe \cdot G_{Fe}^{0} + x_Ti \cdot G_{Ti}^{0} + x_N \cdot G_{N}^{0} + RT \{ x_Fe \cdot \ln x_Fe + x_Ti \cdot \ln x_Ti \\
+ x_N \cdot \ln x_N \} + x_Fe \cdot E_{Fe}^{Ti} \cdot (x_Fe - x_Ti)^{ij} \\
+ x_Ti \cdot E_{Ti}^{N} \cdot (x_Ti - x_N)^{ij} + x_Fe \cdot E_{Fe}^{N} \cdot (x_Fe - x_N)^{ij} \\
\times (x_Fe - x_N)^{ij}.
\] (1)

In this equation, \(G_i^{0}(i=Fe,Ti,N)\) denotes the Gibbs energy functions of the constituent elements Fe, Ti, and N, respectively, which have been generalized into the Scientific Group Thermodata Europe (SGTE) database. \(L_i^{(i)}\) represents the interaction parameter between elements \(i\) and \(j\), and the subscript in this case refers to the solution behavior as regular \((i=0)\) or subregular \((i=1)\). These parameters can be obtained through the Gibbs energy function of the bcc phase in the binary systems. \(x_j\) is the mole fraction of element \(Fe\), Ti, or N, respectively. \(R\) is the gas constant and \(T\) is temperature. In addition to disordered solution phases, some binary compounds may also form ternary phases. For example, FeN is a binary compound in the Fe–N binary with a certain range of homogeneity and its Gibbs energy function is constructed based on the two-sublattice model of (Fe)(N, Va). “Va” refers to vacancy, which is introduced to describe the nonstoichiometric homogeneity range of FeN. Similarly, TiN is described by the model of (Ti)(N, Va). Since both phases have the fcc structure, in the extrapolation, the thermodynamic energy function can be calculated. In the following, the Fe–Ti–N will be used as an example to show how the Gibbs energy function of a ternary phase can be extrapolated from the lower-order systems. If this ternary system is considered as a higher-order system, the lower-order systems of interest are three binary systems: Fe–Ti, Ti–N, and Fe–N. Three categories of phases exist in these three binaries: disordered solution phases and compound phases with and without homogeneity ranges. For example, the Fe solid solution phase based on the bcc structure belongs to the category of disordered solution phases, while Fe2N and FeN are compound phases with and without homogeneity ranges, respectively. The Gibbs energy function for each phase in these three binaries was well modeled in terms of extensive experimental data and they were directly applied to extrapolate the Gibbs energy function of the phase in the Fe–Ti–N ternary system. Several methods exist to determine the extrapolation formula. Hillert analyzed various extrapolation methods and recommended the use of the method of Muggianu et al.

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+ x_N \cdot \ln x_N \} + x_Fe \cdot E_{Fe}^{Ti} \cdot (x_Fe - x_Ti)^{ij} \\
+ x_Ti \cdot E_{Ti}^{N} \cdot (x_Ti - x_N)^{ij} + x_Fe \cdot E_{Fe}^{N} \cdot (x_Fe - x_N)^{ij} \\
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descriptions of these two phases will be combined into one, i.e., (Fe,Ti)(N,VA). For other binary compounds such as Fe2N, it is treated as a purely binary-compound phase since there is no counterpart in the Ti–N binary system. Using the methodology described above, the Gibbs energy function of each phase in the Fe–Ti–N system can be obtained. These Gibbs energy functions will be used to calculate the phase diagram of Fe–Ti–N.

All constituent binaries of the (Co, Ni, or Fe)–M–N (M=Al, Ti, Ta, Nb, V, and B) systems have been thermodynamically modeled and the Gibbs energy function of each binary phase is available from the literature. The references are listed in Table III. They were used to develop the Gibbs energy function of each ternary phase in the (Ni, Fe, Co)–M–N ternary systems. It should be mentioned that the phase diagrams in this study were calculated solely from the extrapolated Gibbs energy functions and the existence of the possible ternary compounds were also ignored. The uncertainties induced by such simplifications will be discussed in the next section. All the calculations in this study were carried out using PANDAT.42 The extrapolated thermodynamic descriptions consider the variation of the phase equilibrium versus both temperature and homogeneity range of each phase. By coupling the extrapolated thermodynamic descriptions of Co–, Ni–, and Fe–M–N with the use of PANDAT, the phase equilibria at any temperature and composition can be calculated for any section.

RESULTS AND DISCUSSIONS

Since the focus of the current thermodynamic evaluation is the thermal stability between ferromagnetic electrodes and the nitride barrier at low temperatures, only the phase equilibria involving solid phases were presented in this paper (i.e., reactions between solid and gaseous species were ignored). With the thermodynamic descriptions of the Co–, Ni–, and Fe–M–N systems developed in this study, isothermal sections over a range of temperatures from 298 to 800 K were calculated. Since typical operation temperatures for MTJs do not exceed 600 K, only isothermal sections at 550 K are presented in this article. This temperature is low enough not to exceed the operating temperature of the device, but is reasonably high to help reach equilibrium. However, the analysis of the interfacial thermal stabilities based on the calculated isothermal sections at 550 K was found to be valid over the full temperature range from 298 to 800 K.

As previously mentioned, in order for an interface to be considered thermodynamically stable, two conditions must be met. One is that a stable phase equilibrium must exist between Co, Ni, or Fe and the candidate tunnel barrier, the other is that there must be negligible mutual solubility, meaning that the candidate tunnel barrier must not dissolve significant amounts of Co, Ni, or Fe and vice versa. With the calculated isothermal sections for (Co, Ni, or Fe)–M–N systems, the thermal stability of the interfaces between Co, Ni, or Fe ferromagnets and the candidate nitride barriers will be discussed as follows. Isothermal sections of ferromagnet–M–N (M=Al, B, Nb, Ta, Ti, and V) at 550 K are shown in Figs. 1–3, respectively. The shaded region in gray denotes that at least one of the phases in equilibrium has a certain range of homogeneity. The isothermal sections in Figs. 1–3 show that stable phase equilibria between ferromagnets and metal nitrides exist in all the investigated systems, meaning that all systems meet the first condition required for a thermodynamically stable interface. Next, we want to examine the mutual solubility between the ferromagnets and these

<table>
<thead>
<tr>
<th>TABLE III. References of binary thermodynamic parameters.</th>
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<tbody>
<tr>
<td>Co–M</td>
</tr>
<tr>
<td>Co–Al</td>
</tr>
<tr>
<td>Co–B</td>
</tr>
<tr>
<td>Co–Nb</td>
</tr>
<tr>
<td>Co–Ta</td>
</tr>
<tr>
<td>Co–Ti</td>
</tr>
<tr>
<td>Co–V</td>
</tr>
</tbody>
</table>

FIG. 1. Isothermal sections of Co–M–N (M=Al, B, Nb, Ta, Ti, and V) at 550 K.
metal nitrides. Based on the homogeneity range of metal nitrides and that of the ferromagnets, the interfaces can be classified into four categories. In the first category, the phases connecting the phase equilibria of Co–AlN, Co–BN, Co–TaN, Ni–BN, Ni–TaN, Fe–BN, and Fe–TaN have stoichiometric ratios with negligible homogeneity ranges. Therefore, the interfaces represented by these phase equilibria meet both conditions and are considered to be thermodynamically stable. The second category includes the Co–NbN, Co–TiN, Fe–NbN, and Fe–TiN interfaces, which feature nitrides that have a certain range of homogeneity along the M–N binary but the solubility of M in the ferromagnet phases is very small. This feature means the nitrides with a range of N concentrations may be formed into tunnel barriers that are in equilibrium with the ferromagnets. This category does not contradict the second condition for a stable interface, but nitride barriers with different N concentrations have nonuniform distributions of electric properties, which may cause nonuniform barrier heights throughout the barrier of the MTJs. However, this is a good feature in terms of the flexibility of adjusting the junction resistance of the tunnel barrier. The interfaces represented by the phase equilibria of Co–VN, Ni–AlN, Ni–NbN, Ni–TiN, Ni–VN, and Fe–AlN are classified into the third category, in which certain amounts of M are found in the ferromagnetic materials. Ferromagnets in this category are prone to intermix with M, which may degrade the intended magnetic properties. The fourth category only contains the Fe–VN interface, which is featured by the mutual solubility between Fe and V in both the ferromagnet phase and the metal sublattice of the metal nitride phase. Whether Fe dissolves into the VN barrier or V into the Fe ferromagnet, device performance will deteriorate and therefore this material is highly undesirable in real applications. In summary, based on the two conditions of phase equilibrium and low mutual solubility between ferromagnets and MN or M, the interfaces in the first or second categories, i.e., Co/AlN, Co/BN, Co/NbN, Co/TaN, Ni/BN, Ni/TaN, Fe/BN, Fe/NbN, Fe/TaN, and Fe/TiN, considered thermodynamically stable. Furthermore, these calculated results confirm the usefulness of some MTJs such as Co/BN/Ni, which were identified as potential MTJs through experimental methods. Ferromagnetic layers in the real MTJs are usually in alloy form such as CoFe and NiFe. By considering the calculated stable interfaces in the ternary systems, the interfaces of CoFe/BN, NiFe/BN, CoFe/NbN, CoFe/TaN, NiFe/TaN, and CoFe/TiN are expected to have good thermodynamic stability.

We have just discussed the importance of phase equilibria between ferromagnets and metal nitrides for thermodynamically stable interfaces. This, in addition to other concerns that we will now address, leads us to claim that our evaluation for interfacial stability serves as the step in preselecting suitable tunnel barrier materials in MTJs for detailed study. The calculations presented in this study are based on bulk thermodynamic information. In thin films, the contributions of strain and interfacial energy may lead to unwanted reactions. Other than interfacial energy and strain energy,
some ternary compounds such as Co$_2$N$_2$M$_4$ or Co$_2$NM$_4$ (Ref. 43) may also form at high temperatures in some systems. However, they are not included in this calculation due to lack of thermodynamic information of these ternary compounds. This simplification is not expected to affect the currently proposed stable interfaces since none of these ternary compounds were observed to change the existing phase equilibrium between ferromagnets and metal nitrides in literature. 44

As we mentioned before, the Gibbs energy function of a ternary phase is solely obtained through extrapolation, no ternary interaction parameters were considered, and therefore this simplification may pose some uncertainties on the solubility range of N in ferromagnets and ferromagnets in nitrides MN. However, even with these limitations, the thermodynamic prediction based on bulk equilibrium data is useful as a tool to cull unsuitable tunnel barrier materials and identify the best candidates for detailed study.

**ACKNOWLEDGMENTS**

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42 PANDAT, software package for multicomponent phase diagram calculation, Computherm LLC, 437 S. Yellowstone Dr. Madison, WI 53719, USA, 1999.