The Formation of Intermetallic Phases by Solid-Phase Reaction of Fe/Al Multilayers

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Abstract. Thin film multilayers of Fe and Al with thicknesses ranging from 10 nm/2 nm to 10 nm/420 nm Fe/Al are used as starting structures to produce intermetallic phases by solid-phase reaction during high-vacuum thermal annealings. By measuring the relative concentrations of the reacting Fe and Al species nearby the growing interfaces and using the recently introduced concept of effective heat of mixing of binary thin-film metallic systems, a method is suggested to predict the phases to be obtained from different combinations of initial multilayer thickness and annealing temperature.

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The rapid expansion of microelectronic technology motivated a great deal of research and development work in the field of interdiffusion and reaction in metal-metal and metal-semiconductor thin-film structures.

One remarkable finding in these studies was that interdiffusion and reaction in thin films could be observed at a much lower temperature than in bulk couples. This is due to the cleanliness of the interfaces between thin films, highly defective microstructures, and better detection sensitivity in thin-film analytical techniques. The low-temperature and the film-thickness limitation on diffusion distance impose a kinetic constraint on thin-film interdiffusion. Consequently, new phenomena in thin-film interdiffusion were found that were not apparent in bulk interdiffusion studies. In intermetallic compound formation, the stable compounds tend to form sequentially, i.e. they grow one by one in thin film bilayers, instead of several or all of them growing together as in bulk cases. Another recently discovered phenomenon is that metastable compounds or amorphous alloys can be formed by interdiffusion upon slow heating using thin film samples [1–5].

Thin-film transition-metal aluminides, in particular, are of great interest to the microelectronics industry due to the prevalence of Al, or one of its alloys, as metallizations [6]. Important properties of Al include low resistivity and good adhesion to SiO₂ and silicate glasses. A diffusion barrier is required to separate the Al metallization from the Si contact in order to avoid spikes of the junction at device processing temperatures. Most of the actual or candidate diffusion barriers consist of, or have as a component, a transition metal. Typical lengths for the reacted layers are 0.1 μm.

The subject of thin-film aluminides has been recently reviewed by Colgan [7]. As with metal-silicon binary systems, with metal-aluminium binary systems there are usually several intermetallic equilibrium aluminide phases. It was not yet possible to predict from first principles which aluminide phase will grow initially in thin-film reactions. It is generally believed that phase formation in thin films is governed more by the kinetics and moving species rather than by the thermodynamic driving forces. However, in a very recent publication, the prediction of phase formation sequence in binary metal-aluminum thin-film systems was rather consistently approached by Pretorius et al. [8] introducing the effective heat of formation concept, which enables the calculation of heats of formation as a function of the relative concentrations of the two atomic species, namely aluminium and the transition metal.

By definition, according to [8] the effective heat of formation ΔH' is

\[ \Delta H' = \Delta H^\circ \times \left( \frac{\text{effect. concent. limit. elem.}}{\text{compound concent. limit. elem.}} \right), \]

where ΔH^\circ is the heat of formation (the change in enthalpy during the reaction at temperature T) for the intermetallic compound being considered, and the numerator in the parenthesis is the relative concentration of the limiting element nearby the growth interface.

On the basis of this definition the prediction of phase formation obeys the following rules:

i) **first-phase formation** — the first compound phase to form during metal-metal interaction is the phase with the most negative, effective heat of formation (ΔH') at the concentration of the lowest temperature eutectic (liquidus) of the binary system;
after first-phase formation in metal-metal binary systems, the next phase to form at the interface between the compound phase and remaining element is the next phase richer in the unreacted element, which has the most negative effective heat of formation.

These rules are shown in [8] to predict several first-phase aluminate formation for many metal-aluminium thin-film systems, as long as the effective concentrations of the two reacting species at the growth interface are approximately determined.

In the above mentioned review article by Colgan [7] it is said that the Fe–Al binary thin-film system reported results on phase formation by the present authors and by Csandidy and colaborators [9,10] were contradictory. The contradictions may be attributed to differences in the initial (bi- or multilayer) thin-film structures, where different Fe to Al ratios are used as well as different total thicknesses. There are, however, more fundamental reasons for the observed discrepancies. One is the fact that the heats of formation of many Fe–Al intermetallic compounds and also for several other Fe–Al phases are very similar, being all around \(-26 \text{kJ/g \cdot atom}\). This fact has as a consequence that very small variations on the concentration of the reacting elements around the growing interface or even small variations of other parameters will lead to different phases being formed. Another reason for the discrepancies is the existence of metastable and quasicrystalline phases in the Fe–Al system which may disrupt the rules of the equilibrium phase diagram.

The present work was undertaken to investigate the formation of intermetallic phases during interdiffusion and reaction occurring in Fe–Al multilayered thin-film structures induced by thermal annealing in high-vacuum. The temperature range between 523 K and 623 K was chosen for the annealings because interdiffusion was shown previously to set in around 520 K in the Fe–Al bilayers [9]. By working with multilayers one can have a better control upon the initial composition nearby the growth interfaces as well as more clear analyses of the interdiffusion of the moving species.

Since the heats of formation of most of the equilibrium phases of the Fe–Al system are very similar, the probability of each of these phases to be effectively formed at a certain annealing temperature should depend very strongly on the relative concentrations of the reacting species nearby the interfaces. In order to explore this dependence a range of relative thicknesses of the individual Fe and Al layers was chosen, from 10/2 nm Fe/Al to 10/42 nm Fe/Al keeping the total thickness of all the multilayers around 100 nm.

Figure 1 and Table 1 are presented here to give an idea of the multilayer parameters and the dependence of phase formation on these parameters. In Fig. 1 are shown the conversion electron Mössbauer spectra (CEMS) of the Fe/Al 10/6 nm and 10/42 nm multilayers as-deposited and annealed during 1 h at different temperatures in a ultra-high vacuum furnace. The dotted lines are the experimental points and the solid lines represent the best fits with the parameters given in Table 1. The source was \(^{57}\text{Co}\) in a Rh matrix.

**Table 1.** Mössbauer parameters used to fit the experimental points of the 10/6 and 10/42 nm Fe/Al multilayers shown in Fig. 1. The isomer shifts \(\delta\) are given with respect to \(\alpha\)-Fe. \(\Delta E_Q\) is the magnitude of the quadrupole interaction and \(\Gamma\) the linewidths. The compound phase attributed to each set of Mössbauer parameters are obtained by comparison with the results existing in the literature according to the references given in the last column. This is a preliminary phase characterization. A far more complete determination of the phases will be made in a forthcoming publication, based on combined CEMS and X-ray diffraction analyses. Typical errors of all the parameters are 10%.

<table>
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<th>(T) [K]</th>
<th>(\Delta E_Q) [mm s(^{-1})]</th>
<th>(\delta) [mm s(^{-1})]</th>
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<td>0.31</td>
<td>FeAl(_6) [15]</td>
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</table>

Fig. 1. Conversion electron Mössbauer spectra of the 10/6 nm and 10/42 nm multilayers as-deposited and annealed during 1 h at different temperatures in a ultra-high vacuum furnace. The dotted lines are the experimental points and the solid lines represent the best fits with the parameters given in Table 1. The source was \(^{57}\text{Co}\) in a Rh matrix.