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Thermochimica Acta 348 (2000) 53–59

thermochimica acta

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Nb/Al and Nb/Al(Cu) multilayer thin films: the enthalpy of formation of $NbAl_3$

G. Lucadamo[a], K. Barmak[b,*], S. Hyun[a]

[a]Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA
[b]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Received 4 August 1999; received in revised form 6 December 1999; accepted 7 December 1999

Abstract

Using differential scanning calorimetry (DSC), the heat of formation of $NbAl_3$ was measured from the reaction of sputter-deposited Nb/Al and Nb/Al(Cu) multilayer thin-films with different bilayer thickness. The measured heat of reaction of the Nb/Al samples was 40.0±4.1 kJ/g-atom. The Nb/Al(Cu) films, with 0.5 and 1.0 wt.% Cu, yielded heats of formation of 40.8±0.5 and 40.5±0.6 kJ/g-atom, respectively. The measured heats of reaction in all three sets of samples were consistent with earlier investigations and revealed that, within experimental errors, the addition of the small amounts of Cu did not affect the formation enthalpy of $NbAl_3$. Thus, combining the data from all three types of samples gives a value of 40.6±2.9 kJ/g-atom for this enthalpy. Enthalpy measurements as a function of multilayer periodicity further indicated that no significant interdiffusion or intermixing took place prior to $NbAl_3$ formation. This lack of intermixing was also confirmed by fabricating a multilayer sample with a 10 nm thick codeposited layer, having a nominal composition of $Nb_{42}Al_{58}$, interleaved between the Nb and Al layers. The presence of this intentionally intermixed layer caused a reduction in reaction enthalpy to 33.1±0.5 kJ/g-atom. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thin-film; Nb/Al; $NbAl_3$; Differential scanning calorimetry; Formation enthalpy

1. Introduction

The study of solid state reactions in thin-film transition metal aluminide and silicide systems continues to attract considerable interest. This attention is a result of the prevalence of thin-film reactions in microelectronics metallization that requires detailed knowledge of thermodynamic and kinetic reaction parameters in order to determine optimum processing conditions such as annealing temperatures and times. Differential scanning calorimetry (DSC) has proven to be an effective technique to obtain the relevant kinetic and thermodynamic parameters for solid state reactions in thin films. Indeed, a recent review has highlighted the application of DSC to the study of thin film reactions [1].

Among existing studies of thin films, constant heating rate DSC investigations of Ni/Al multilayer thin films are particularly applicable to the present work [2,3]. Films with bilayer thickness (Λ)<20 nm showed a single exotherm, whereas in multilayers with Λ>20 nm, two separated exothermic peaks were observed. Ex-situ X-ray diffraction (XRD) studies found that both peaks were due to the formation of

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[*] Corresponding author. Tel.: +1-412-268-4380; fax: +1-412-268-3113.
E-mail address: katayun@andrew.cmu.edu (K. Barmak)

PII: S0040-6031(99)00512-2

the $NiAl_3$ phase. By integrating the total area beneath these two peaks, a value for the enthalpy of formation of $NiAl_3$ was determined. For films with $\Lambda > 300$ nm, the enthalpy was close to that reported for the formation of $NiAl_3$ in bulk samples. However, as the bilayer period of the film decreased, the total enthalpy measured from the reaction of the multilayers was reduced rapidly. Analytical models used to calculate the reduction of enthalpy found that a chemically diffuse interface provided the best agreement with the experimental heats of reaction. This was presumably due to the observed formation of NiAl at the interfaces during deposition. By using the model, the multilayer enthalpy data was extrapolated to infinite periodicity to give the bulk heat of formation of $NiAl_3$ as 37.9 ± 0.5 kJ/g-atom [1]. This value should be compared with the literature value of 37.7 ± 2.1 kJ/g-atom [4]. The excellent agreement between the extrapolated value for the model and the experimentally measured bulk heat of formation of $NiAl_3$ suggests that thin films may be used in thermodynamic investigations of other compound-forming systems.

In this work, we have studied the Nb/Al system using multilayer thin films with a range of bilayer thickness. This system also is characterized by two-peaked phase formation, but differs from the Ni/Al system in that no phases are observed prior to the formation of equilibrium $NbAl_3$ [5–8]. The effects of dilute Cu additions (0.5 and 1.0 wt.%) on the reaction enthalpy are also investigated. We compare our measurements with existing calculated and experimentally determined values of formation enthalpy of $NbAl_3$ reported in the literature [9–11].

2. Experiment

2.1. Film deposition

Since free-standing films offer better signal-to-noise ratios, they are preferred over films on substrates for the determination of reaction and formation enthalpies. The signal-to-noise ratio can be further improved by employing a multilayer architecture, thus increasing the number of reacting interfaces present in the thin-film sample. The most suitable free-standing thin-film calorimetry samples are either obtained by depositing films that delaminate from the substrate or by using a sacrificial underlayer that can be fully removed from the film.

In order to investigate the impact of the underlayer on our measurements, Nb/Al multilayer films for DSC analysis were deposited on both photoresist and on Cu. Silicon wafers (8 cm diameter, (100) orientation) were coated with ~1 mm of Shipley #1827 photoresist or ~200 nm of sputter-deposited Cu. The photoresist was spun onto the wafer and subsequently baked to prevent the outgassing when placed into the sputtering system.

For Cu underlayers, both Si wafers and glass slides were used as substrates. The slides were first cleaned ultrasonically at room temperature in acetone followed immediately by ethanol for ~3–5 min in each solution. Copper films were deposited at 500 W using DC magnetron sputtering in a UHV system with a base pressure typically $<7 \times 10^{-7}$ Pa. Ar (99.9995%), passed through a purifier to remove residual O_2 and H_2O before entering the chamber, was used as the sputtering gas. The sputtering pressure was 0.4 Pa controlled by a capacitance manometer. Deposition rates were calibrated by measuring the thickness of calibration films using a Tencor P-2 contact profilometer. To ensure uniform thickness, substrates were rotated at ~10 RPM during deposition. The deposition rate was determined from the average of 16 independent thickness measurements distributed over the surface of the wafer. Each measurement was taken from an average of five scans with a scan-to-scan reproducibility of ±0.1 nm. Film thickness typically varied by 1–2% over the surface of the wafer for the targets used in this study. Additional variations in deposited layer thicknesses could be introduced by target erosion during sputtering. As a result, the sputtering rates were recalibrated every fourth or fifth multilayer run. The Cu deposition rate was determined to be ~0.4 nm/s for the above conditions.

The Nb/Al samples were deposited immediately after deposition of Cu on Si substrates. However, the Cu coated glass slides, which were used for the Nb/Al(Cu) alloys, were first removed from the vacuum system and exposed to air. The Al(Cu) alloy films were deposited from alloy targets with the nominal compositions of 0.5 and 1.0 wt.% Cu. The purity and composition of all of the sputter targets are listed in Table 1. For transmission electron micro-

Table 1
Listing of targets and purity

Target material	Purity (%)
Al	99.999
Nb	99.95
Al-0.5 wt.% Cu	99.999 each
Al-1.0 wt.% Cu	99.999 each
Cu	99.999

scopy (TEM) studies, films were also deposited on oxidized Si (100) wafers.

As mentioned before, multilayer architecture was employed to maximize the number of interfaces in the sample and to provide adequate DSC signal. Total multilayer thicknesses were 1 μm. The films consisted of a half layer of Al on the top and bottom surfaces to provide equivalent reaction conditions at all interfaces while protecting the Nb layers from oxidation during DSC experiments. The values of Λ including the individual elemental layer thicknesses (chosen to maintain a molar ratio of 1Nb:3Al) are listed in Table 2.

All of the multilayers were deposited at 250 W DC. The deposition rates were measured as before yielding values for Nb of ~0.09 and ~0.1–0.15 nm/s for the Al and Al(Cu) alloys. The substrate temperature was estimated to be <373 K during deposition. Some samples checked by quantitative electron probe micro-analysis using wavelength dispersive spectroscopy (WDS) indicated a maximum deviation of ~4 at.% for each element from the desired stoichiometry of 75 at.% Al (or Al(Cu)) and 25 at.% Nb.

2.2. DSC and TEM sample preparation

After deposition, films were removed from the substrate for DSC analysis. To decrease the time required to dissolve the Cu underlayer, the films were first scribed into ~2.5 cm×2.5 cm sections. Then the Si wafers or slides were placed in a 9:1 solution of HNO_3 and distilled water to minimize Al attack [12]. The Cu layer was dissolved within 10–20 min if the Cu was exposed to air. The unexposed Cu took significantly longer, sometimes several hours. The films were successively rinsed for several minutes in three separate beakers containing distilled or deionized water. The free-standing films were then placed in a fourth beaker with distilled or deionized water for ~3 h after which they were transferred directly to a beaker containing ethanol. The films were removed and allowed to dry for ~12 h. After removal, the films retained a highly reflective surface. If the multilayer films were attacked by the acid, the surface acquired a dark grey color.

Table 2
Nominal multilayer sample periods and individual layer thicknesses

Λ (nm)	t_{Al}, $t_{Al(Cu)}$ (nm)	t_{Nb} (nm)
23.2	17	6.2
72	53	19
143	105	38
333	245	88

For films on photoresist, the photoresist was dissolved and films were rinsed in distilled water several times before a final rinse in ethanol. The films were then allowed to dry overnight. Some of the film samples were cleaned in a UVOCS UV/O_3 cleaner to remove the organic residue left on the surface. The cleaning time was 15 min per side.

Cross-sectional TEM samples were prepared by mechanical polishing and dimpling techniques to obtain a thickness of <10 mm in a manner similar to that described in [13]. Final thinning to electron transparency was accomplished by ion polishing from one side in a Gatan 691 precision ion polishing system.

2.3. DSC and TEM experiments

Calorimetry was performed using a Perkin–Elmer DSC 7. The baseline parameters were adjusted to obtain a reproducible heat signal over the temperature range of the reactions of interest (323–1000 K). This is the most difficult and critical adjustment necessary for obtaining accurate reaction enthalpies due to the large temperature range needed to encompass the entire Nb/Al reaction.

The temperature calibration was performed by measuring the melting onset temperature of In and Zn. Three different tangent constructions were used to determine an average onset temperature. The thermal lag factor for the instrument was determined by running a Zn sample at 10, 40, and 80 K/min. Zn was used for this calibration since its melting point of 692 K is closest to the reaction temperatures of Nb and Al. This resulted in a maximum deviation in temperature of +1.8 K at 80 K/min. Zn was also used to calibrate the enthalpy measurements. An average enthalpy of 108.78 ± 0.18 J/g was determined from the melting of the Zn calibration sample. This value is in excellent agreement with the theoretical enthalpy of 108.37 J/g. Finally, a Pb sample was run to verify the temperature and enthalpy calibration.

For the next step, the dried, free-standing films were placed in an envelope made by folding a 10 mm×10 mm×0.025 mm piece Pt foil (99.99%). The foil was first weighed using a calibrated balance to the nearest 10^{-5} g. Averages of at least three measurements were used to determine the weight and in most cases the average of five were used. Approximately 2–3 mg of film was then added and the foil and film were re-weighed. Again, the actual weight was determined from an average of five separate measurements. A reference piece of Pt foil was prepared and its weight matched to within 0.1 mg of the first Pt foil (without film). The envelopes were carefully sealed by folding and flattened to ensure good thermal contact with the DSC furnace base; this step resulted in a final sample size of ~4 mm×4 mm.

The folded Pt foils were loaded into the calorimeter furnaces which were evacuated using a rotary vacuum pump for ~30 min. The furnaces were then repeatedly purged with ultra high purity Ar (99.9995%). The Ar gas was then permitted to flow through the furnaces for 10 min. while the DSC signal stabilized. The flow rate of the Ar was controlled by an upstream flow meter to 20 ml/min. The specimen was then heated from 323 to 993 K at a heating rate of 40 K/min. After the run was completed, the DSC was allowed to stabilize for ~30 min. The Nb/Al reaction is irreversible, therefore, the baseline for each run was established by running the same heating program a second time without disturbing the sample or reference. By subtracting this baseline curve and dividing by the mass of the sample, the enthalpy of the reaction was determined.

TEM specimens were observed using a JEOL 2000 FX microscope operating at 200 kV. The cross-sectional samples were oriented so the beam was along the (110) zone axis of the Si substrate and, therefore, perpendicular to the cross-section.

3. Results and discussion

Besides a precise weight measurement, the accurate determination of the heat of formation requires a repeatable baseline that matches the evolved heat signal at the beginning and end of the scan. In the case of photoresist underlayers, the baseline never matched at high temperatures due to residual resist. Although UV O_3 cleaning reduced the baseline discrepancy, it did not eliminate it. Therefore, for determination of the enthalpy data, the calorimetric traces were not used for films deposited on photoresist underlayers.

Fig. 1 shows a series of baseline-subtracted DSC curves obtained from free-standing 1Nb/3Al multilayer samples with $\Lambda=72$, 143, and 333 nm heated at 40 K/min. By integrating the area under the two peaks in the calorimetry data and normalizing by the sample weight, the enthalpy of the reaction was determined for bilayer thicknesses ranging from 20 to 333 nm and two Cu concentrations. Table 3 summarizes the enthalpy associated with the formation of NbAl$_3$ from current and previous measurements. Note again that

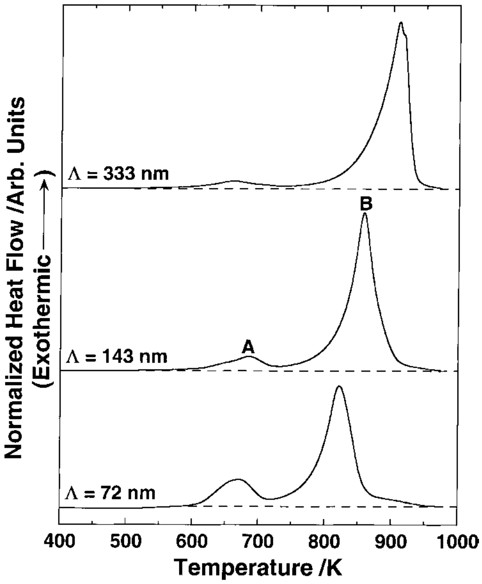

Fig. 1. A series of baseline-subtracted DSC curves taken from free-standing, $\Lambda=72$, 143, and 333 nm 1Nb/3Al multilayers heated at 40 K/min that were obtained by dissolving a Cu underlayer in 90% HNO$_3$. Both peaks A and B correspond to the formation of NbAl$_3$.

Table 3
Comparison of the heat of formation of $NbAl_3$

Sample type	Method	ΔH (average, kJ/g-atom)	Number of meas.	Ref.
Nb–Al alloy	Knudsen cell effusion	32.6±2.1		[8]
Evaporated Nb–Al multilayers (Cu underlayers)	calibrated DTA	42.5±7.5		[9]
Nb and Al powders	direct synthesis calorimetry	40.5±0.6		[10]
N/A	FP-LMTO[a]	41.5		[11]
Sputter-deposited Nb/Al-0 wt.% Cu multilayers	DSC	40.0±4.1	8	this work
Sputter-deposited Nb/Al-0.5 wt.% Cu multilayers	DSC	40.8±0.5	2	this work
Sputter-deposited Nb/Al-1.0 wt.% Cu multilayers	DSC	40.5±0.6	6	this work
All multilayers combined	DSC	40.6±2.9	16	this work

[a] The linear-muffin-tin-orbital (LMTO) method in the full potential (FP) approximation.

the current measurements reported in the table were determined from several samples with different *N*. The number of samples used to determine the average enthalpy also varied depending on the quality of the baselines. The net area under the peaks was taken from the temperature at which the heat signal began to deviate from the baseline to the temperature where the baseline and heat signal rejoined at the completion of the reaction. For the Nb/Al reaction these measurements were taken from ~573 to 973 K and the Nb/Al(Cu) samples were ~473–973 K.

The error on an individual measurement was never more than 0.8 kJ/g-atom due primarily to the error in weighing the sample. The scatter in the data is, in part, due to deviations from stoichiometry. Taking the heat of formation as 40 kJ/g-atom and a deviation of ±4 at.%, could account for measured values as low as 36 kJ/g-atom. The larger scatter in the Nb/Al samples as compared to Nb/Al(Cu) is expected to be a consequence of the longer exposure of these samples to acid, and thus possible incorporation of hydrogen into the Nb layers. This further highlights the importance of the type and method of preparation of the sacrificial underlayer.

Comparing the results for Nb/Al with those for Nb/Al(Cu) shows that within experimental error, the small additions of Cu do not affect the formation enthalpy of $NbAl_3$. In other words, the presence of dilute concentrations of Cu in Al is not influencing the thermodynamics of the system, as may have been expected.

Considering the available past and present measurements, the enthalpy of formation of $NbAl_3$ obtained from the Knudsen cell effusion measurement is clearly low in comparison. The values obtained from DTA experiments, while accurate, exhibit larger errors. The errors in these measurements, in addition to run-to-run variations, are due to the errors in the calibration constant *K* and *C*, the heat capacity and thermal conductivity of the DTA apparatus, respectively [9]. These calibration constants are required to convert the temperature difference measured in the DTA to power in order to calculate the heat released by the reaction. In contrast, DSC measurements in the Perkin–Elmer instrument eliminate these errors by directly measuring the power evolved by the reaction resulting in a more precise value. The formation enthalpy data obtained in our study also compare favorably to that of Meschel and Kleppa measured by direct synthesis calorimetry [10]. It is also worth noting that all of the experimental measurements, except the Knudsen cell effusion measurement, agree well with the value calculated using the linear-muffin-tin orbital method [11].

By plotting the heat of formation values versus bilayer period or layer thickness the extent of interdiffusion or compound formation prior to phase formation can be ascertained. Fig. 2 shows such a plot for the Al/Nb samples. The values for the heat of formation are observed to be relatively constant within the error, this indicates that significant interdiffusion does not occur in this system. This result differs from systems such as Al/Ni, discussed in Section 1, where the formation of a compound during deposition causes a pronounced decrease in the total heat of the reaction [2].

The effect of intermixing on the heat of formation of $NbAl_3$ was then investigated in more detail. Another multilayer film was deposited with a 10 nm thick

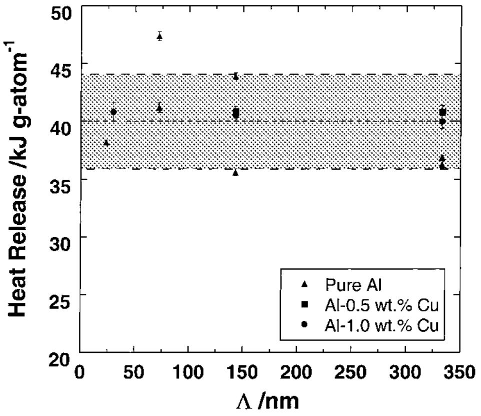

Fig. 2. Plot of reaction enthalpy (ΔH) versus bilayer period (Λ) for a series of 1Nb/3Al films with the Al containing 0, 0.5, and 1.0 wt.% Cu. The constant value of ΔH indicates that intermixing does not occur in significant amounts in this system. The dashed line and scatter-band indicate the average and standard deviation, respectively, of the formation enthalpy of $NbAl_3$ obtained from the pure Al multilayers.

codeposited alloy layer with a composition of $Nb_{42}Al_{58}$, as estimated from the relative deposition rates of Nb and Al at 250 W. X-ray diffraction of this alloy revealed a broad peak indicative of an amorphous, disordered, or nanocrystalline phase. This sample simulated the effect of a 10 nm intermixed layer at each of the reactant interfaces. The reaction enthalpy was measured from this sample to be 33.1±0.5 kJ/g-atom.

The relationship between heat of reaction (ΔH) of a sample and the heat of formation for a compound (ΔH_f) for a certain amount of intermixing is given by [1,14]:

$$\Delta H = \Delta H_f\left(1 - \frac{4\omega}{\Lambda_{\text{eff}}}\right) \tag{1}$$

where ω is the half-thickness of the intermixed layer and L_{eff} is the effective bilayer thickness. This equation assumes an intermixed region with a sharp composition profile. In a multilayer sample with an interleaved codeposited layer an effective period, L_{eff}, is defined as (Fig. 3):

$$\Lambda_{\text{eff}} = \Lambda + 2t_{\text{NbAl}} \tag{2}$$

For a multilayer with Λ=72 nm, Λ_{eff}=92 nm. Substituting the values for Λ, ω (5 nm) and using the values measured from DSC for ΔH_f, Eq. (1) yields a heat of reaction (ΔH) of 31.3±3.1 kJ/g-atom. This value is close to the heat of reaction measured directly from calorimetry for the samples with the codeposited layers. Conversely, if the heat of formation measured from the DSC is substituted for ΔH, ω can be calculated. This yields a value of 8±3 nm which is in reasonable agreement with the codeposited layer thickness.

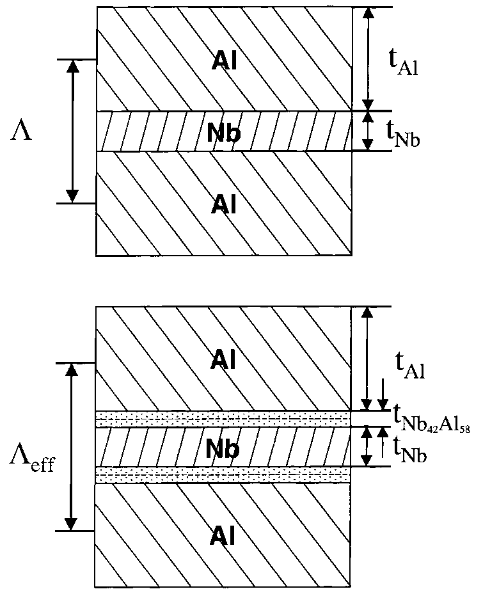

Fig. 3. Schematic drawings of a typical multilayer film and a film with an interleaved co-deposited layer showing the effective periodicity (Λ_{eff}) used in Eq. (1).

Quantitative analytical electron microscopy experiments have also shown that the interface width in a Λ=333 nm Nb/Al multilayer was <5 nm with a sharp interlayer transition [15]. The apparent lack of significant intermixing or reaction in the Nb/Al films may result from the small atom size difference (~3%) between Nb and Al and the possibility of granular epitaxy during growth of these films. This epitaxy is evident in the as-deposited microstructures where columns of grains aligned in similar orientations are observed to propagate through several bilayers (Fig. 4). This is not observed in Ni/Al films where the atom size difference is 13%, resulting in incoherent interfaces that can lead to increased intermixing. Previous studies have in fact indicated that a large atom size difference can lead to increased intermixing or the formation of disordered interfaces [16]. The fiber

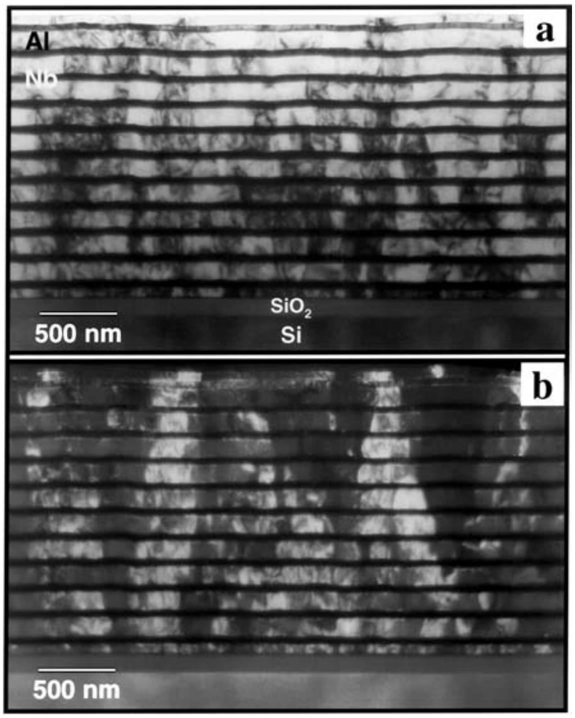

Fig. 4. (a) Bright-field transmission electron microscopy image of the cross-section of a 1Nb/3Al multilayer with Λ=143 nm. (b) Centered-dark field image using Al (111) and Nb (110) reflections showing that grains of similar orientation propagate through the thickness of the multilayer.

texture of the Nb and Al layers is also evident in X-ray diffraction measurements which indicate the predominance of the Nb(110) and Al (111) peaks [7]. At sufficiently low Λ (<10 nm) superlattice peaks have been observed in Nb/Al multilayers [7,17,18].

4. Conclusions

By using a sacrificial Cu underlayer that is dissolved in a 9:1 HNO_3: H_2O solution, free-standing films of Nb/Al and Nb/Al(Cu) were obtained for the determination of the heat of formation for the compound $NbAl_3$. The heat of formation data obtained from the multilayers in this study agreed well with data available in the literature. Finally, no significant decrease in enthalpy was observed with decreasing bilayer thickness suggesting that interfacial intermixing or interdiffusion does not readily occur in this system during film deposition. This could be due to the formation of coherent interfaces between the Nb and Al layers.

References

[1] C. Michaelsen, K. Barmak, T.P. Weihs, J. Phys. D 30 (1997) 3167.
[2] K. Barmak, C. Michaelsen, G. Lucadamo, J. Mater. Res. 12 (1997) 133.
[3] C. Michaelsen, G. Lucadamo, K. Barmak, J. Appl. Phys. 80 (1996) 6689.
[4] R. Hultgren, R.L. Orr, P.D. Anderson, K.K. Kelley, in: Selected Values of Thermodynamic Properties of Metals and Alloys, New York, Wiley, 1963.
[5] Y. Im, P.E. Johnson, L.T. McKnelly Jr., J.W. Morris Jr., J. Less-Common Met. 139 (1988) 87.
[6] K. Barmak, K.R. Coffey, D.A. Rudman, S. Foner, J. Appl. Phys. 67 (1990) 7313.
[7] K. Barmak, C. Michaelsen, S. Vievekanand, F. Ma, Phil. Mag. A 77 (1997) 167.
[8] I. Shilo, H.F. Franzen, R.A. Schiffman, J. Electrochem. Soc. 129 (1982) 1608.
[9] K.R. Coffey, K. Barmak, D.A. Rudman, S. Foner, J. Appl. Phys. 72 (1992) 1341.
[10] S.V. Meschel, O.J. Kleppa, J. Alloys Compounds 191 (1993) 111.
[11] C. Colinet, A. Pasturel, D. Nguyen Manh, D.G. Pettifor, P. Miodownik, Phys. Rev. B 56 (1997) 552.
[12] H.H. Uhlig, R.W. Revie, Corrosion and Corrosion Control, 3rd Ed., Wiley, New York, 1985, p. 350.
[13] J. Bravman, R. Sinclair, J. Elec. Micro. Tech. 1 (1984) 53.
[14] T.P. Weihs, T.W. Barbee, M.A. Wall, J. Mater. Res. 11 (1996) 1403.
[15] G. Lucadamo, M. Watanabe, K. Barmak, D.B. Williams, C. Michaelsen, R. Alani, Phil. Mag. A. 79 (1999) 1423.
[16] B.M. Clemens, T.C. Hufnagel, J. Alloys Compounds 194 (1993) 221.
[17] D.B. McWhan, M. Gurvich, J.M. Rowell, L.R. Walker, J. Appl. Phys. 54 (1983) 3886.
[18] J.R. Baumann, E.K. Liebemann, M. Simon, E. Bucher, Phys. Rev. B 45 (1992) 3778.