ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 225–228

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

H- and D distribution in metallic multilayers studied by 3-dimensional atom probe analysis and secondary ion mass spectrometry

P. Kesten*, A. Pundt, G. Schmitz, M. Weisheit, H.U. Krebs, R. Kirchheim

Institut für Materialphysik, Universität Göttingen, Hospitalstrasse 3–7, D-37073 Göttingen, Germany

---

Abstract

Pd/Nb- and Fe/V multilayers were prepared by either ion sputtering or laser ablation. They were deposited on tungsten tips for field ion microscopy using the 3-dimensional atom probe. D was added by doping from the gas phase. In agreement with thermodynamic data D is accumulated in the metal with the more negative heat of solution, i.e. V or Nb. However, SIMS depth profiles of H concentration measured at room temperature show a pronounced enrichment in the top regions of both Nb- and V layers. This is also observed in a deuterium depth profile obtained by the 3d atom probe measured at 60 K despite the moderate removal of atoms by field evaporation which does not give rise to the formation of lattice defects when compared to sputtering. Thus we assume that surface segregation is the reason for H/D accumulation in surface near regions. The effect vanishes if measurements by the atom probe were made at 20 K where the D mobility is too low to allow D transport to the surface during the time of measurements. With the superior depth resolution of the 3d atom probe being less than 0.5 nm we were able to show that at both the V/Fe and the Nb/W interface depletion of deuterium occurs in a range of about 0.5 nm within the Nb- or V layer due to intermixing of adjacent metals.

Keywords: Metals; Thin films; Metallic multilayers; Laser deposition; Ion sputtering; Hydrogen absorption; Tomographical atom probe

---

1. Introduction

With the enormous progress in the preparation and analysis of metallic multilayers with chemical modulations on a nanometer scale, the behavior of hydrogen in these systems has also attracted intensive research [1]. Besides the strain effects in thin films and multilayers electronic effects at the interfaces are proposed that change the hydrogen solubility in thin films compared to bulk. During investigations of the hydrogen uptake of Mo/V [2] and of Fe/V [3] superlattices Hjörvarsson et al. discovered that compared to bulk vanadium the V layers absorbed less hydrogen the thinner they were. This observation was interpreted as an interface effect caused by a charge transfer from Mo and Fe, respectively, to V. The decreased hydrogen solubility could be described quantitatively by a so-called ‘dead’ layers with zero H solubility and a thickness of two to three monolayers. The hydrogen concentration was measured using the $^{1}H(^{15}N, \alpha\gamma)^{12}C$ nuclear resonance reaction. Since the spatial resolution of this method is about several nanometers the dead layers could not be resolved and the mean hydrogen concentration of the V layers having different thickness was measured instead. In order to determine the local hydrogen distribution with a better resolution on a subnanometer scale we measured hydrogen concentrations using a 3-dimensional atom probe in combination with a field ion microscope [4]. In addition, time of flight–secondary ion mass spectrometry (TOF–SIMS) [5] was applied.

2. Experimental procedure

Pd/Nb- and Fe/V multilayers were prepared by either ion sputtering or laser ablation. Multilayers with single layer thickness of 1 to 10 nm were deposited on Si substrates for secondary ion mass spectrometry (SIMS) and on needle-shaped W substrates (tip radius 30–100 nm) for field ion microscopy (FIM) [6,7]. In the case of laser ablation, mixing processes are expected due to the high energies of the deposited ions being about 100 eV [8]. In order to prepare metallic multilayers with reduced intermixing ion sputtering was used. But due to their large misfit f.c.c. Pd and b.c.c. Nb multilayers could not be prepared by ion sputtering with a sufficient mechanical stability for the tomographic atom probe (TAP) analysis

---

*Corresponding author. Tel.: +49-173-5283392; fax: +49-69-1330-5405-648.

E-mail address: philipp@kesten-onlin.de (P. Kesten).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01596-1

where large electric fields exert considerable mechanical forces on the samples. Nevertheless, we succeeded in preparing stable multilayer packages with ion sputtering using V and Fe both b.c.c. with a small misfit of the bulk metals of 5.5%.

SIMS measurements were performed with a Cameca TOF IV SIMS. For multilayer analysis Cs- and Ga ion beams with energies of 1 keV and 12 keV were used for sputtering and analyses, respectively.

FIM was performed using the tomographic atom probe (TAP) [9]. With this method single atoms from the surface of the sample are removed by applying high voltage pulses and identified chemically by time-of-flight measurements. The original positions of evaporated and ionized atoms on the specimen surface are determined by measuring the impact of the ions on a two-dimensional position sensitive detector and taking the simple projection geometry into account. The projection geometry can be calculated from the initial radius and the shaft angle of the tip, the evaporation voltage and the element specific evaporation field strength [10]. The 3d-reconstruction of the detected atoms can be analysed concerning the local distribution of the elements.

Deuterium was used in the TAP measurements because hydrogen gas and hydrocarbons within the residual gas of the vacuum system lead to a considerable background signal for hydrogen. The multilayers were first degassed at 473 K and then loaded at room temperature from the gas-phase with D_2 pressures ranging from 1 to 20 mbar. The samples for the SIMS measurements were loaded with hydrogen electrochemically which allows to adjust the hydrogen concentration in the multilayers precisely.

3. Results and discussion

The reconstruction [4] of a Pd/Nb multilayer is shown in Fig. 1. Concentration profiles are determined by calculating local concentrations in probe volumes of the reconstructed data. In Fig. 2 the Pd and Nb concentration in the Pd/Nb multilayer of Fig. 1 is presented. Each concentration was calculated for a 0.24-nm-thick slice of the cylinder shown in Fig. 1 which had a cross-section of 28 nm^2 and a length of 22 nm. The average number of atoms in each slice was larger than 100 giving rise to a statistical error of less than 20% of the concentration value.

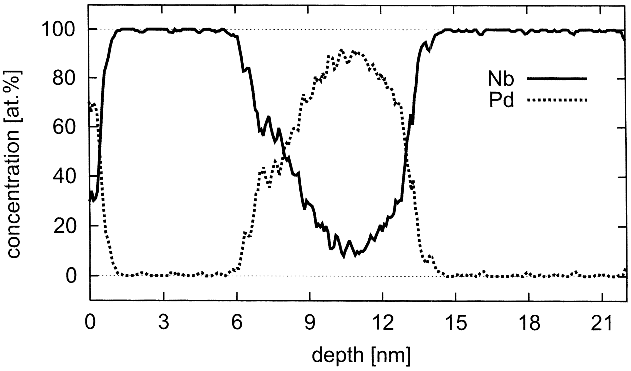

Fig. 2. Pd- and Nb concentration profile through the analysed volume shown in Fig. 1. Concentrations were calculated from atomic ratios within slices of the cylinder shown in Fig. 1. The cylinder had a radius of 3 nm and the slices were 0.24 nm thick. Thus each slice contained about 200 atoms (the detector efficiency being about 50%) and the relative statistical error is about 20%.

In the prepared sample an asymmetric intermixing is observed at the Pd/Nb- and the Nb/Pd interface in the concentration profile of the multilayers (cf. Fig. 2), as expected from the kinetic energy of the particles during pulsed laser deposition and the different implantation depth of both elements. After loading the Pd/Nb multilayer with 12 mbar D_2, the concentration profile obtained by TAP measurements performed at 60 K shows a D depletion at the Nb/W interface over a thickness of about 0.5 nm (Fig. 3). This is about the region where the interface mixing occurs and Nb is alloyed with W (cf. Fig. 3).

Fig. 4 shows the concentration profile of a sputtered

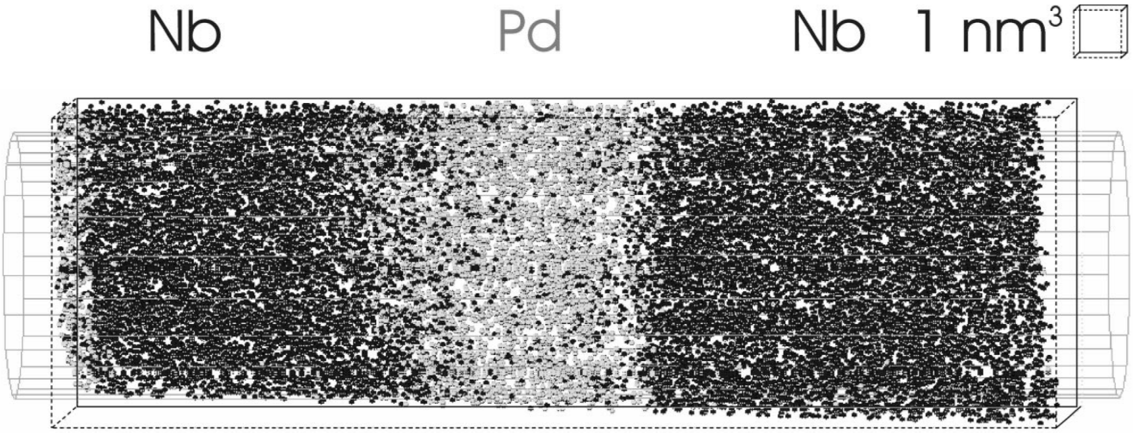

Fig. 1. Result of a tomographic atom probe analysis of a Nb/Pd multilayer produced by laser ablation. Positions of Nb- (dark dots) and Pd atoms (grey dots) are shown within the analysed volume of 7×7×22 nm^3. Atoms within the shown cylinder are used for the evaluation of the concentration profile shown in Fig. 2.

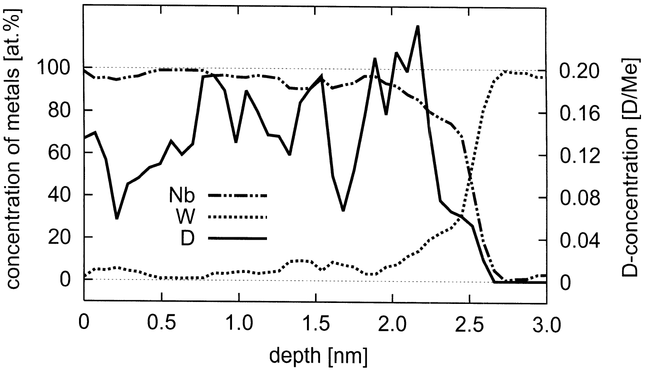

Fig. 3. Similar concentration profile as the one shown in Fig. 2 but for a sample which was exposed to 1.9 mbar of D_2 gas for 23 h at room temperature. Pd- and Nb layers were peeled off by the electric field and, therefore, only the remaining Nb/W interface could be analyzed. Note that the depletion of D at the interface is accompanied by alloying of the Nb with W.

Fe/V multilayer deposited on W and capped with Pd. The profile shows a sharp Fe/W interface and an intermixing at the Fe/V interfaces extending over a range of 1–2 nm.

Fig. 5 shows the concentration depth profile of a different Fe/V multilayer prepared the same way as the one in Fig. 4 but annealed at 473 K for 12 h and than exposed to 2.5 mbar D_2 for several hours at room temperature. Interdiffusion of the metal atoms at the higher temperature is negligible and, therefore, the concentration profiles of the metal atoms at the interfaces did not change. The profile in Fig. 5 was measured with the TAP at 60 K. In agreement with thermodynamic data D is accumulated in the V layers. From the heats of solution the ratio of hydrogen solubility between V and Fe can be estimated to be $c_H(V)/c_H(Fe) \approx 10^{10}$. D is enriched at the Fe/V interface and decreases continuously towards the V/Fe interface. This asymmetrical shape emerges as an effect of D transport to the continuously formed fresh surfaces (see following discussion). In measurements performed with a Fe/V double layer at 20 K no D depletion is observed towards the V/Fe interface (Fig. 6).

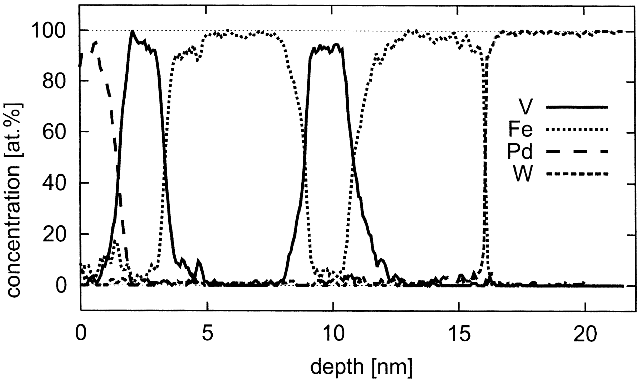

Fig. 4. Same as Fig. 2 but for V/Fe multilayers with a Pd-cap layer prepared by sputtering the metals onto a W-tip.

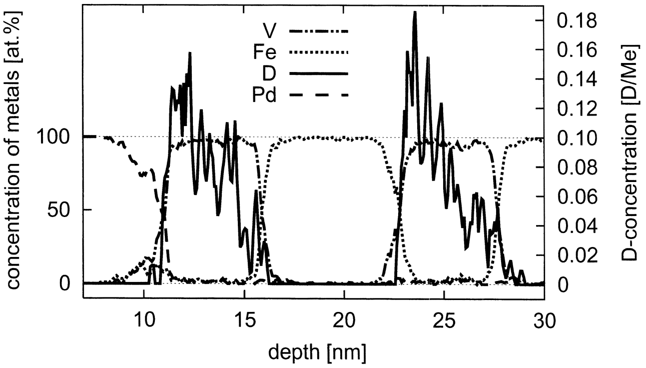

Fig. 5. V/Fe multilayer prepared as the one shown in Fig. 4 with an additional exposure to deuterium gas for several hours at room temperature under a partial pressure of 2.5 mbar. The TAP analysis was conducted at 60 K. Deuterium is absorbed by the vanadium layers due to its most negative heat of mixing compared to Fe and Pd. D concentration decreases from the Fe/V interface towards the V/Fe interface which is explained by continuous surface segregation during the field evaporation of the sample. Because of the smaller number of D atoms within the slice used for the evaluation of concentrations the statistical error becomes significant.

The effect of surface segregation visible in Fig. 5 is caused by the high mobility of deuterium in combination with the destructive nature of the experimental technique. It is known that hydrogen in metals occupies surface- and subsurface-sites preferentially [11]. The principle of the TAP is to analyze the removed surface atoms of the sample. By removing the surface atoms hydrogen can segregate in the freshly built surface and subsurface sites and, therefore, being depleted in deeper regions of the layer. To achieve the equilibrium concentration any diffusion process has to be suppressed during the measurement. In the case of deuterium, temperatures of 20 K seem to be sufficient to suppress D diffusion. SIMS depth profiles at room temperatures were measured to confirm this model. The SIMS technique is a surface removing technique, too [5]. A pronounced hydrogen enrichment was found in the surface regions of the samples [12]. Hydrogen segregation on the surface near regions during SIMS measurements

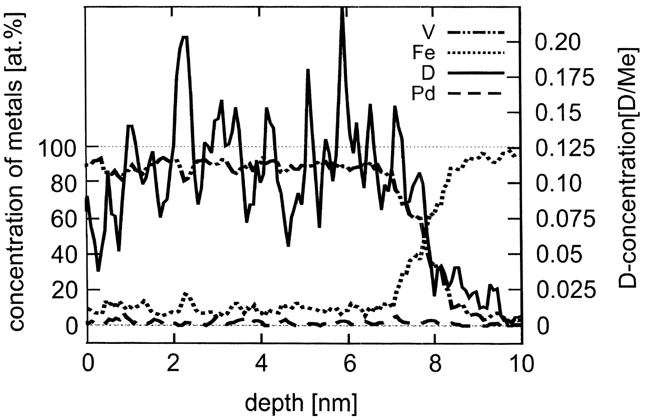

Fig. 6. Same as Fig. 5 but with an analysis temperature of 20 K. The decrease of D concentration towards the V/Fe interface is no longer visible.

were also reported by Züchner and co-workers [13]. They explained the phenomenon by an increased defect density at the surface area caused by the primary ions having high energies. We have observed an analogous phenomenon with the TAP despite the moderate removal by the field evaporation process that does not give rise to the formation of lattice defects when compared with sputtering. We assume that during the continuous removal of atoms from the sample a fresh surface is formed and deuterium (and/or hydrogen) is segregating to this surface, because the binding energies of H atoms to metallic surfaces are larger when compared to the bulk. Thus D atoms are diffusing towards the surface because it is acting as a sink.

The effect vanishes at 20 K. This is in agreement with a diffusion length being smaller than the layer thickness at 20 K. The diffusion length was calculated from extrapolated D diffusion coefficients measured at higher temperatures. The reduced D mobility at the very low temperatures allows the determination of equilibrium D concentrations in the multilayers. Under these circumstances a constant D concentration is measured inside the V layer (Fig. 6). The depth profile shows an intermixing of V and Fe over a range of about 2 nm at the interfaces. In this region the D concentration decreases from 0.11 D/Me in the V layer to 0 D/Me in the Fe layer. Depth profiles with the TAP of Nb/W interfaces (cf. Fig. 3) show similar results. At 20 K a constant D concentration is observed inside the Nb film, which compared to W is the metal with the more negative heat of solution. Again at the Nb/W interface a decrease of the D concentration is observed only in regions of intermixing. At elevated temperatures D segregates to the surface of the Nb films because of the high mobility of D in Nb.

According to band structure calculations for binary alloys [14] a decrease of D concentration in metals is expected if they are alloyed with a metal having a smaller affinity to hydrogen. Thus a reduced solubility ratio can be expected at V/Fe- and Nb/W interfaces in regions of intermixing.

4. Conclusions

Measurements of hydrogen in metallic multilayers with the 3-dimensional atom probe are to our knowledge the first ones that provide data of the local distribution on a subnanometer scale together with the concentrations of the host metals. The results for Fe/V multilayers show, like the results for the Nb/W systems [7], a decrease of D concentration in the V- or Nb layers near the V/Fe- or Nb/W interface, respectively, caused by an intermixing of the adjacent metal atoms. This intermixing can be determined in a region of 1–2 nm at the interface (Fig. 4). Therefore hydrogen depletion at the interfaces is most probably chemically induced in contradiction to the suggestion of a dead layer caused by intermixing of electrons [2,3]. With a TAP analysis of multilayered systems having a smaller region of intermixing, i.e. metallic components with a positive heat of mixing, the existence or absence of this electronic effect could be elucidated more clearly.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (KI-230/19) is gratefully acknowledged.

References

[1] B. Hjörvarsson, G. Andersson, E. Karlsson, J. Alloys Comp. 253–254 (1997) 51, and Refs therein.

[2] B. Hjörvarsson, J. Ryden, E. Karlsson, J. Birch, J.-E. Sundgren, Phys. Rev. B 43 (8) (1991) 6440.

[3] G. Andersson, B. Hjörvarsson, P. Isberg, Phys. Rev. B 55 (3) (1997) 1774.

[4] T. Al-Kassab, H. Wollenberger, G. Schmitz, R. Kirchheim, High Imaging and Spectroscopy of Materials, Springer–Verlag, Berlin, 2000, in press.

[5] A. Benninghoven, F.G. Rüdenauer, H.W. Werner, Secondary Ion Mass Spectroscopy, John Wiley and Sons, New York, 1987.

[6] P. Kesten, PhD Thesis, University of Göttingen, (2000), in German, (http://webdoc.sub.gwdg.de/diss/kesten).

[7] P. Kesten, A. Pundt, G. Schmitz, R. Kirchheim, (in preparation).

[8] S. Fähler, H.-U. Krebs, Appl. Surface Sci. 96 (1996) 61.

[9] D. Blavette, B. Deconihout, A. Bostel, J. Sarreau, M. Bouet, A. Menand, Rev. Sci. Instrum. 64 (11) (1993) 2911.

[10] T. Jeske, G. Schmitz, Appl. Phys. Lett., (submitted for publication).

[11] K. Christman, Mol. Phys. 66 (1989) 1.

[12] P. Kesten, M. Weisheit, A. Pundt, G. Schmitz, H.-U. Krebs, R. Kirchheim, (in preparation).

[13] J. Scholz, H. Züchner, H. Paulus, K.-H. Müller, J. Alloys Comp. 253/254 (1997) 459.

[14] R. Griessen, T. Riesterer, Hydrogen in Intermetallic Compounds I, Topics in Applied Physics, Vol. 63, Springer-Verlag, Berlin, 1988.