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Technologically important coatings of transition-metal aluminides can be produced by thermal or ion beam mixing of multilayer structures sputter deposited on substrates. The quantitative detection of constituents by depth profiling is sufficient to establish the efficiency of mixing methods. However, to decide whether a mixture of nanoparticles or a stoichiometric alloy is formed, EXAFS analysis of the local atomic neighborhood in the film is required. Ni K edge EXAFS spectra are measured on a series of samples of Ni/Al multilayer on Si(111) surface, after ion mixing at different substrate temperatures. The spectra show that with increasing temperature the nickel aluminide phase gradually substitutes the Ni fcc metal phase.

1. Introductiom

Deposition of thin films of intermetallic compounds has attracted considerable attention in the past two decades due to possible application in microelectronics, metallurgy and medicine (Colgan, 1990). Methods used for preparation of the coatings include physical vapour deposition, ion implantation, ion beam mixing, controlled heating of multilayers and plasma-enhanced diffusion (Mozetič *et al.*, 1996; Drobnič *et al*, 1996; Miracle, 1993; Massalski *et al.*, 1990; Kattelus *et al.*, 1988; Ma *et al*, 1989; Krafcsik *et al*, 1983; Tardy *et al*, 1985; Ball *et al*. 1987).

In the present paper we study the formation of a thin layer of stoichiometric NiAl alloy on a silicon substrate. The coatings are prepared by subsequent deposition of thin layers of aluminum and nickel, using a sputtering system (Mozetič *et al.*, 1996). The multilayer structure is then thermostated and exposed to high-energy ions to obtain a uniform coating due to the ion beam mixing.

The diffusion of Ni atoms into the Al matrix in the treatment has been established by Auger electron spectroscopy (AES). The method, however, cannot tell whether the diffused component remains in separate nanoparticles of pure metal or whether the desired NiAl alloy is formed. X-ray diffraction is of little help, since at temperatures below 670 K the coatings do not relax into the long-range order. We used EXAFS signal of Ni atoms to analyse the atomic structure of the Ni/Al coatings.

Ni K-edge EXAFS spectra were measured in total electron yield (TEY) mode on six Ni/Al multilayer coatings prepared on the Si 111 monocrystal surface and treated with ion-beam mixing at different substrate temperatures. The spectra were interpreted with the help of EXAFS spectra of pure Ni metal and of NiAl monocrystal.

2. Experiment.

The Ni/Al multilayers were sputter deposited on smooth silicon (111) substrates in a Baltzers Sputron apparatus. The thickness of individual Ni and Al layers was 25 nm and 38 nm, respectively. The thickness was measured during deposition with a quartz microbalance so that an overall stoichiometric ratio of 1:1 could be maintained. The composition of the sample was determined by AES depth profile analysis with the scanning Auger microprobe (Physical Electronics Ind SAM 545 A).

The samples were treated with ion-beam mixing in Baltzers MPB 202 RP ion implanter using 350 keV Ar^+ ions at the dose of 1×10^{16} ions/cm^2. The substrate temperature during the treatment was kept constant: six points in the range from 128 K to 603 K were chosen.

Ni K-edge spectra of the Ni/Al multilayers and reference samples were recorded at the XAS13 experimental station of the DCI storage ring at LURE, Orsay (France), using the Si(111) channel cut monochromator. Detection with the total electron yield (TEY) technique at liquid nitrogen temperature probed the samples to the depth of about 100 nm. The absorption spectra are given by the ratio of the TEY detector current and the current provided by the ionisation cell, which monitors the incident photon flux. The standard stepping progression within 1000 eV region of the Ni K-edge was adopted.

3. Results and discussion

The AES depth profiles of three samples are shown in Fig. 1. Local atomic concentration of constituents is plotted against sputtering time. The plot does not show true layer thickness because of different sputtering rates of Ni and Al. However, the periodicity of the bilayers in the as-deposited sample is evidently fairly uniform.

The plots demonstrate the efficiency of the mixing and its dependence on the substrate temperature. At 503 K, some vestiges of the original layers still remain, while at 553 K (and above) the mixing is complete, and the multilayer is completely homogenized.

EXAFS analysis is performed with the University of Washington programs using FEFF6 code for ab initio calculation of scattering paths (Rehr et al., 1992; Stern et al., 1995). The EXAFS oscillations were extracted from the absorption spectra using the standard treatment by AUTOBK procedure of the UWXAFS package. The spectra of the Ni/Al thin film coatings are shown in Figure 2, together with spectra of the reference Ni foil and NiAl monocrystal samples.

The basic facts about the structure can be deduced already from the Fourier transforms (Fig. 3), even before the detailed quantitative analysis is performed. The series of the FT spectra shows that there is indeed a change from the pure fcc Ni structure in the as-deposited multilayer, to the NiAl binary alloy structure after the application of the ion mixing.
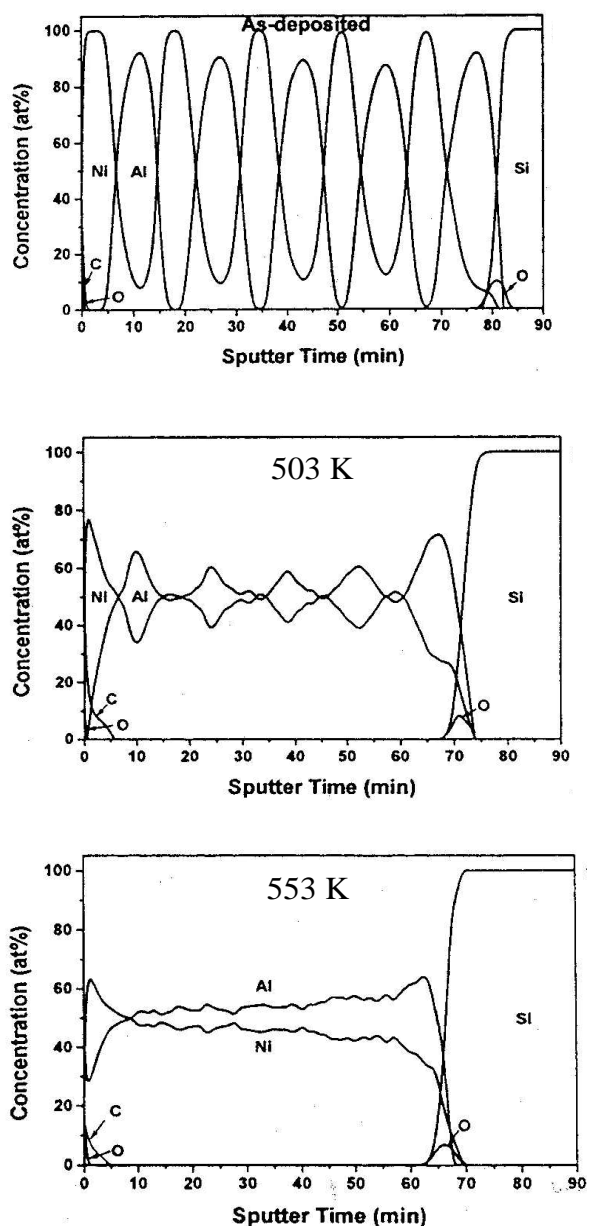
Figure 1
AES sputter profiles of the as-deposited Ni/Al multilayer structure, and of samples after ion mixing at substrate temperatures of 503 K and 553 K.

Quantitative EXAFS analysis is used to determine the ratio of the two phases in each coating. FEFF models based on crystal structures of Ni metal (fcc with the lattice constant a = 3.5239 Å, (Wyckoff, 1963) and NiAl binary alloy (CsCl structure with lattice constant of a = 2.88 Å (Kittel, 1971) are constructed. The Ni atom surrounding begins with 12 and 6 neighbours in Ni fcc lattice in consecutive shells at distances of 2.49 Å, 3.52 Å, while in NiAl crystal structure the first two neighbor shells contain 8 Al atoms at 2.49 Å and 6 Ni atoms at 2.88 Å.
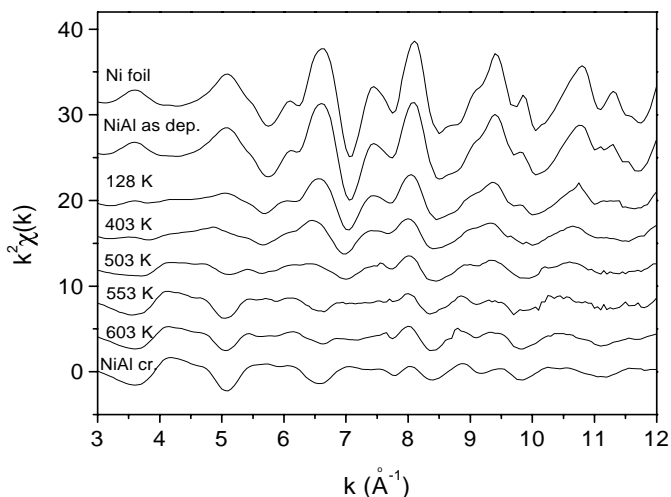

Figure 2
Ni K-edge EXAFS spectra measured on the as deposited Ni/Al multilayer sample and of samples after ion mixing at temperatures 128 K, 403 K, 503 K, 553 K and 603 K. For comparison the spectra of Ni metal and NiAl monocrystal are added.
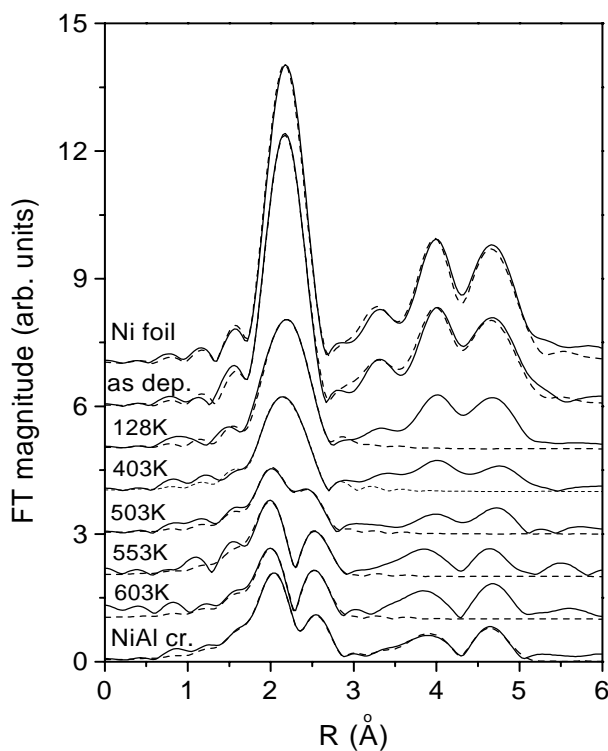

Figure 3
Fourier transform magnitudes of Ni K-edge EXAFS spectra measured on the as deposited Ni/Al multilayer sample and on samples after ion mixing at temperatures 128 K, 403 K, 503 K, 553 K and 603 K. For comparison the spectra of Ni metal foil and NiAl monocrystal are added. Experiment – solid line; fit – dashed line.

The parameters of the FEFF models are calibrated by the Ni foil and NiAl monocrystal spectra, giving an excellent fit for the region from 1.5 Å to 5.0 Å with minimum number of variable parameters for each model: the lattice expansion ($\Delta r/r$), the

amplitude reduction factor (S_o^2), the width (σ^2) for the first (first two for NiAl) neighbour shell(s), and Debye temperature (TD) governing the D. -W. factors of all remaining paths (Stern *et al.*, 1995). The shell coordination numbers and relative radii are fixed at their crystal structure values.

The environments of Ni atoms in the two crystal structures differ so much, that the analysis of the nearest neighbours up to 3 Å is sufficient to identify the amount of each phase in the treated samples.

The treated Ni/Al coatings are described by a superposition of the two models. The fixed value of S_o^2 (=0.78(5)) and coordination numbers of each structure are retained, while the relative weight is varied together with separate Debye-Waller factors σ^2 and shell radii (Table I). The quality of the fit is shown in Fig. 3.

Table 1

Parameters of the nearest neighbours up to 3 Å from the central Ni atom in the as deposited Ni/Al multilayer sample and in samples after ion mixing at substrate temperatures T 128 K, 403 K, 503 K, 553 K and 603 K.: w – fraction of NiAl crystal phase in the sample; R – neighbour distance, and σ^2 - Debye-Waller factor. For comparison the same parameters for reference Ni foil and NiAl monocrystal are listed. Best fit is obtained with zero-energy shifts ΔE_o of 5(1) eV for Ni in metallic phase and 3(1) eV for Ni in NiAl crystalline phase. Uncertainty of the last digit is given in parentheses.

model	NiAl phase					Ni metal phase	
Sample	w [%]	R_{Al} [Å]	σ_{Al}^2 [Å^2]	R_{Ni} [Å]	σ_{Ni}^2 [Å^2]	R [Å]	σ_l^2 [Å^2]
Ni foil	0	/	/	/	/	2.485(1)	0.0028(5)
Ni/Al As-dep.	0	/	/	/	/	2.487(1)	0.0035(3)
T = 128 K	39(6)	2.49(3)	0.004(2)	/	/	2.49(1)	0.0034(4)
T = 403 K	54(6)	2.47(1)	0.011(5)	/	/	2.51(1)	0.0044(8)
T = 503 K	64(2)	2.50(1)	0.004(1)	2.86(1)	0.017(2)	2.50(1)	0.0037(5)
T = 553 K	86(4)	2.48(1)	0.004(1)	2.85(1)	0.011(2)	2.49(1)	0.003(1)
T = 603 K	79(2)	2.51(1)	0.004(1)	2.86(2)	0.012(2)	2.51(1)	0.002(1)
NiAl crystal	100	2.471(2)	0.0045(6)	2.826(5)	0.0092(8)	/	/

4. Conclusions

It is evident from the table that bombardment with energetic Ar ions results in a mixed neighborhood of Ni atoms at all substrate temperatures, so that a complete segregation of the metals on the nanoscale is definitely precluded. The presence of the nickel aluminide phase, however, is only proved for substrate temperatures above 503 K, where the population of the shell of second-closest Ni neighbors is found in equilibrium with the population of the first-neighbor Al shell. For the two lowermost temperature points, the presence of the first shell of Al neighbors is established, but the results on the corresponding second shell remain indecisive. It is conceivable that the Ni-Al bonds result merely from Ni atoms knocked off into the Al layer, the medium being too cold to relax with diffusion into the stoichiometric NiAl alloy.

At the temperature of 553 K and above, where AES depth profile shows that the mixing of the multilayer structure is complete, EXAFS provides a more detailed picture. It confirms that even in this low temperature range the treatment of the coating leads to predominant nickel aluminide phase. However, about 20% of Ni remains in the metallic fcc phase. Judging from AES profiles it is finely dispersed in the coating.

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