X-ray absorption spectroscopy and X-ray diffraction analysis of crystalline CoTi$_2$ grown by DC co-sputtering: A theoretical and experimental comparison

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Abstract

A series of thin films were grown at 500 ◦C with a Co and Ti base on silico substrate oriented at (4 0 0) by means of the DC co-sputtering technique. For 7 and 11% Co concentrations, 50, 80, and 110W were used. CoTi$_2$ structure was simulated with the FEFF routine of the WinXAS program. XAS analyses were also performed in order to compare simulated results with experimental results. The X-ray diffraction and atomic absorption results reveal a CoTi$_2$ (Fd-3ms) and Ti (P63/*mmc)* phase, while extended X-ray absorption fine structure spectroscopy shows slight variations in the coordination numbers and distances from close neighbors and have 0–7% deviations. The results showed good agreement between the theoretical and experimental results.

Introduction

Recently, interest in the different properties of binary alloy thin films has increased due to the rapid development of thin film growth techniques. These techniques allow the preparation of metals and alloys in several metastable states which sometimes are not obtained with bulk materials. The growth process of thin films is kinetically controlled and occurs outside thermodynamic equilibrium.

The DC co-sputtering technique by balanced magnetron has been used to deposit thin Co and Ti films. Cobalt and its alloys (3d transition metal compounds) are resistant to wear and corrosion even at high temperatures. The high stability of these

alloys is related to the vigorous ionic nature of their metallic bond. This is due to the substantial charge transference of titanium to cobalt atoms, which prevents the formation of a disordered state in these alloys [1]. Co and Ti alloys are stable up to the fusion point. Co and Ti compounds are important components of many industrial alloys. Together with super-alloy applications, a new class of magnetic devices based on Co and Ti are being developed for electronic devices. In literature, there exists information about the CoTi system for concentrations higher than 50% Co, but the material becomes amorphous [2–6]. In particular, the intermetallic phase $CoTi_2$ has a cubic structure CF96, and it is formed by peritectic reaction at 1058 ∘C. Depending on the volume fraction of this phase in the alloy may yield a high strength toweight ratio, strength at moderate temperatures and good resistance to creep and fatigue. For example, the fine grained quasi-eutectoid α-Ti/$CoTi_2$ alloys exhibit superior flow stresses at room temperature of about 1200MPa and superplastic properties over a wide strain rate range of 10^{-5} to 10^{-2} s^{-1} in the temperature range 650–750 ∘C [7].

The objective of the present work was to determine the structure and chemical environment of cobalt in thin films obtained from DC co-sputtering.

In order to carry this out these *ex-situ* analyses were performed such as X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS), a specific element technique which is extremely sensitive to the local environment and produces reliable information about the coordination numbers and distances of first neighbors [8–13].

Experimental details

Thin films of Co–Tiwere prepared at 500 ◦C in an INTERCOVAMEX V3 sputterin system with four magnetrons using DC and pulsed DC power sources. Highly oriented siliconwafers (4 0 0) with an oxidized surface (SiO2) were used as substrate. As it was reported, Co is directly deposited onto a pure silicon surface, even at ambient room temperature; the Co–Si reaction (silicides) usually is crystalline with similar resistances to metals [14, 15]. To avoid this thermal treatment, high vacuum was applied in order to oxidize the substrate.

The thin films, at 7 and 11 wt.% Co concentrations, were deposited by DC cosputtering [16] at 50, 80, and 110W. The DC co-sputtering consisted of covering the surface of a targetwith metal strips, as is shown in Fig. 1. In thiswork, cobaltwafers, in symmetric form in the erosion ring of a 3 in. titanium target, were pasted with silver paint. Then the titanium and cobalt were simultaneously bombarded with argon ions. The distance between the erosion target and the substrate was approximately 200mm. The cobalt was of 99.998% purity and the titanium of 99.995%. The base pressure in the chamber was 2×10^{-6} Torr. Argon (99.995%) pressure was 4mTorr. The thickness of the films was monitored by a quartz crystal detector. Final deposit time was 1 h for all samples. Depositing was started with an argon flow of 7.5 ccpm. The sample was cleaned, with the shutter placed, for 5 min in order to avoid oxide and organic material contamination of the surfaces of both materials.

Chemical composition was determined by means electron dispersion spectroscopy (EDS) in a JEOL model JSM-5800lv scanning electron microscope. Structural characterization was carried out in an X-pert PRO PANANYLITICAL X-ray

diffractometer with a Cu Kα (λ-1.540598 Å) at 0.05◦ steps and 10 s intervals. The X-ray absorption spectra were obtained at ambient temperature in the total electron production mode; which is especially appropriate for thin film materials. X-ray absorption spectroscopy (XAS) analyses were carried out at the Stanford Synchrotron Radiation Laboratory in the seven to three beam line assisted by a fluorescent emission detector due to the low Co concentration. Typical runs lasted about an hour in collecting K-edge absorption data in localized cobalt with an energy of $E - 7.717$ KeV.

All spectra presented one common problem; the resonances of the Si substrate diffraction lines overlapped in the XAS spectrum. However, these diffraction peaks were removed by average interpolation.

Cobalt valence was obtained by comparing the edges of the samples through the use of XANES. The comparison was made with respect to the CoO spectrum. EXAFS was only applied at the ionization edge of the Co through the use of phase transferability. This allowed inferring that the information obtained would be the same if the titanium absorption spectrum were analyzed [17].


Fig. 1. Titanium target (3 in.) with Co wafers/flakes they were pasted with silver paint.

Results and discussion

Small angle X-ray diffraction

Fig. 2 shows the diffraction pattern for the grazing angle of the CoTi/Si1, CoTi/Si2, and CoTi/Si3 films grown at 7% Co concentration. The phases present were, an intermetallic $CoTi_2$ (Fd-3ms) compound of the Cu_2Mg type and Ti (P63/*mmc*) [18]. $CoTi_2$ contains 96 atoms per cell. The compound is formed peritectically at ~1058 ◦C and presents a maximum homogeneity range of ~32.9–33.3 cobalt atomic percent [19]. All cobalt reacts with titanium and the rest forms its own phase. Fig. 3 shows the diffraction spectra for CoTi/Si4, CoTi/Si5, and CoTi/Si6 films grownwith 11 wt.% cobalt concentration. As seen, the phases in this series are the same as the previous case. These results show that the $CoTi_2$ phase grows at the expense of the Ti, which has a high degree of order when the substrate is kept at high temperature during growth.
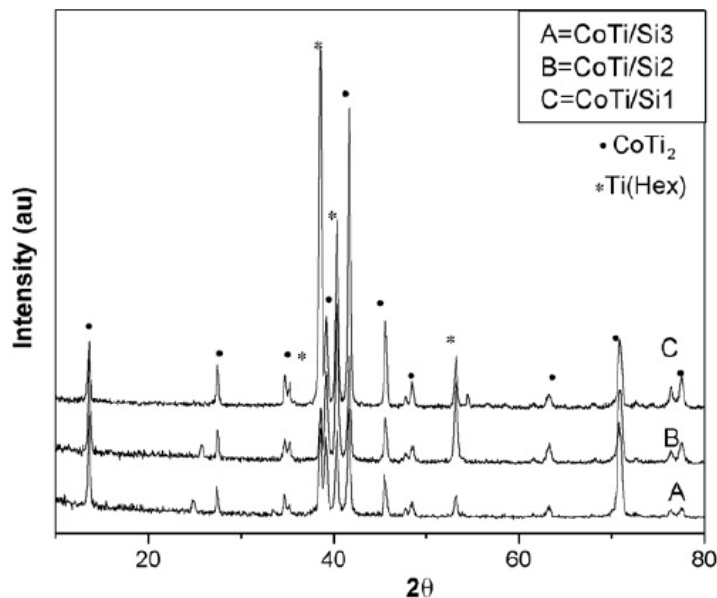
Fig. 2. CoTi/Si1, CoTi/Si2 and CoTi/Si3 diffraction spectra obtained in grazing beam mode. The phases are represented ●, $CoTi_2$ phase; *, Ti (Hex) phase.

EXAFS analysis

On the other hand, in a XAS experiment, the probability that an X-ray photon which comes in contact with the sample will be absorbed by the sample as a function of energy is measured. In the experiment, the incident beam of the photons was gradually increased and the transversal section of the absorption process was measured. The physical mechanism of the XAS experiment was that an atom which absorbs an incident photon and an electron from the deep core should create an unoccupied state that results in an excitation or ionization process.

In order to obtain a simplified EXAFS formula, some approximations were necessary. The first was a dipolar approximation, which describes interactions between deep-core electrons and high-energy X-ray photons well. This approximation allowed us to express the transversal section of absorption as:

$$P_{if} = \frac{2\pi^2 e^2}{m^2 \omega} |M_{if}|^2 \rho(E_f) \tag{1}$$

Where P_{if} is the probability of the transition of the electron from the initial state *i* to the final state *f* with e and m as its charge and mass. $P(E_f)$ is the available states of the electron. ω is the frecuency of the incident photon and $|M_{if}|$ is the dipolar matrix element that relates the transition of the electron from the initial $<i|$ to final $<f|$ state.

By considering the absorption coefficient as proportional to Pif, it is possible to write the theoretical equation for the EXAFS signal [20] as:

$$\chi(k) = \frac{1}{k} S_0^2 \sum \frac{N_i}{R_i^2} \exp(-2\sigma^2 k^2) \exp\left(\frac{-2R_i}{\lambda(k)}\right) |f_i(k)| \sin[2kR + \Phi_i(k)]$$
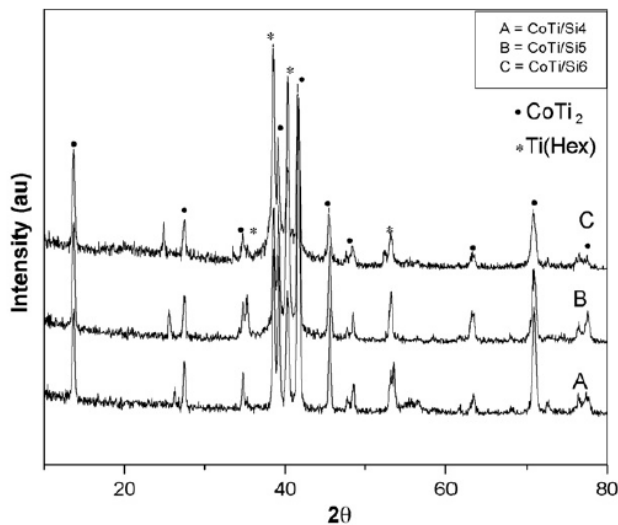
Fig. 3. X-ray diffraction spectrum in small angle mode for the CoTi/Si4, CoTi/Si5 and CoTi/Si6. The phases are represented ●, CoTi$_2$ phase; *, Ti (Hex) phase.
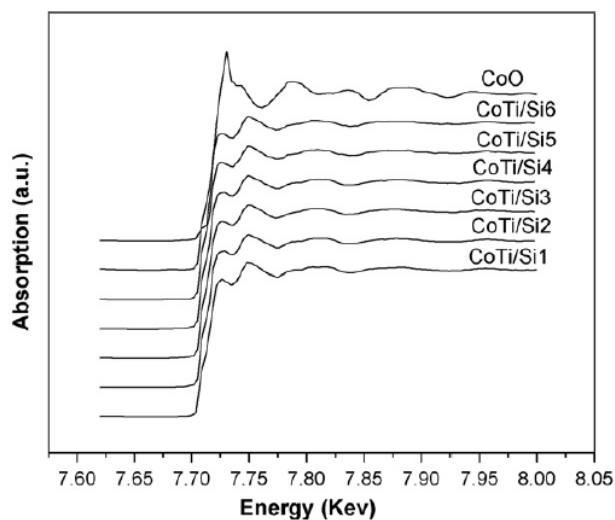

Fig. 4. XANES for Co and Ti films grown by co-sputtering. The position of the en edges for each spectrum coincide with the reference cobalt oxide and which fund with an oxidation state of 2+; therefore, the valence of the cobalt in the CoTi$_2$ p is the same as CoO. The K-edge absorption spectra for Co were normalized.

Eq. (2) calculates $\square$(k), the fractional modulation of the absorption coefficient of X-rays, and explains all the measured or calculated specific interactions for a number of atoms. $\overline{S_0^2}$ accounts for inelastic loss processes. F_i(k) is the energy dependence of the

photoelectron dispersion process. R_i^2 is the distance between the absorber and disperser (Å^2). K is the moduls of the wave vector for the photoelectron (Å^{-1}).

Fig. 4 shows the XAS spectra for the Co K-edge for grown Co and Ti based films. The spectra were numerically processed by means of WinXAS version 3.2 and taking away the background part until normalization. The lowest part of the pre-edge and the absorption spectrumwere removed by fitting it with a polynomial function. By analyzing the absorption spectra for cobalt in the $CoTi_2$ phase, it can be seen that the spectra coincide with the CoO reference spectrum. This indicates that the valence of the Co is the same for both phases (Co^{2+}).

Fig. 5 shows the radial distribution function (RDF) for the six samples. As seen, the shapes of the peaks are slightly different. This is mainly due to the degree in which the distribution of the first neighbors and coordinates affect amplitude and, therefore, the intensity and full width at half maximum (FWHM).

FEFF results

In order to calculate the radial distribution function (RDF), the conversion of the energy space E to the frequency space k through the relation $k^2 = 2m (E-E_0) \hbar^2$ was carried out. Through this conversion, frequencies X(k) were generated by the Fourier transform FT (X(k) k^3); where k^3 is a weight function that prevents EXAFS amplitude dampening.

The fitted composite model was done using the FEFF routine, which uses an ab initio approximation, which is auto-consistent.
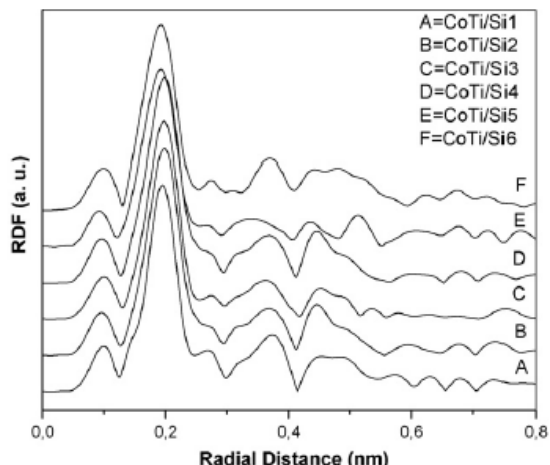
Fig. 5. Radial distribution functions for different grown films. As seen, even when there are two cobalt concentrations a CoTi$_2$ phase is conserved.

The calculations were based on the relativistic Green functions in real space for all the electrons without symmetry requirements. The input for the program was the structural spatial group, its reticular parameters, the absorbing atom and the atomic positions obtained by XRD. FEFF calculates the theoretical RDF of the atom cluster itself and is comparable to experimental FDR. This is a highly iterative process. Fig. 6 shows the fitting between the experimental spectrum (solid red curve) and the cluster generated by FEFF (line of open circles). The rest of the lines are the real and imaginary components of the RDF. As seen, a good fitting was obtained with the exception of a few peaks which were not possible to fit. This was mainly due to the fact that the effect of the thin films themselves was also considered and present residual forces, tension or compression which play an important role in micro-structural details.

Table 1 shows the complete results of the distances of the first neighbors and coordination sphere as well as the fittings. The coordination numbers 12, 4 and 16, had

maximum changes on the order of 9%. The deviations of the distance to first neighbors are within the range of 0–7%.
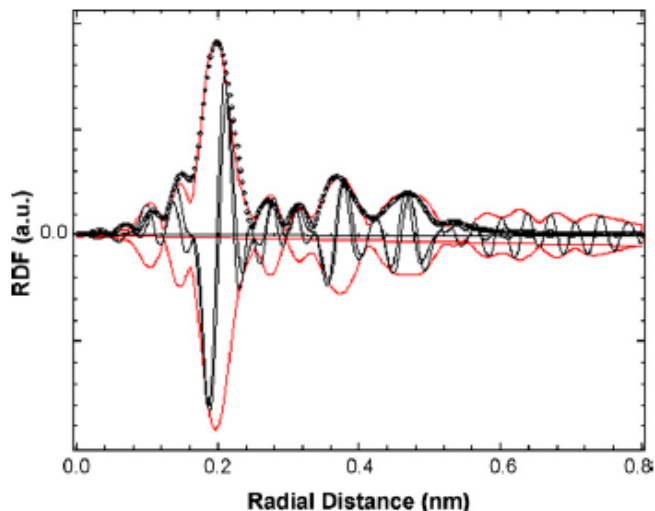
Fig. 6. Fitting of FDR obtained for the theoretical and experimental spectrum of the CoTi/Si1 sample.

Table 1
Results obtained through the adjustment of the experimental spectra with cluster generated by FEFF for the CoTi$_2$ structure

Sample	$R_{adjusted}$ (nm)	$R_{theoretical}$ (nm)	Distance	E_R ($\Delta R/R$)	E_N ($\Delta N/N$)
CoTi/Si1	0.26353	0.27901	Co–Ti	0.05545	0.0993
	0.27906	0.29141	Co–Co	0.04237	0.0150
	0.43741	0.43712	Co–Ti	0.00064	0.0395
CoTi/Si2	0.26485	0.27901	Co–Ti	0.05071	0.0407
	0.27649	0.29141	Co–Co	0.05121	0.0776
	0.46590	0.43712	Co–Ti	0.06582	0.0000
CoTi/Si3	0.26384	0.27901	Co–Ti	0.05435	0.0993
	0.27765	0.29141	Co–Co	0.04722	0.0049
	0.43271	0.43712	Co–Ti	0.01009	0.1266
CoTi/Si4	0.2.6545	0.27901	Co–Ti	0.04859	0.0100
	0.27781	0.29141	Co–Co	0.04669	0.0000
	0.46767	0.43712	Co–Ti	0.06987	0.0303
CoTi/Si5	0.26193	0.27901	Co–Ti	0.06118	0.0303
	0.27549	0.29141	Co–Co	0.05463	0.0000
	0.45281	0.43712	Co–Ti	0.03589	0.0000
CoTi/Si6	0.26225	0.27901	Co–Ti	0.06003	0.0616
	0.27481	0.29141	Co–Co	0.05698	0.0000
	0.41845	0.43712	Co–Ti	0.04271	0.0000

Where E_R and E_N are the relative deviations in the position and the coordination number.

Conclusions

Good-quality films with 7 and 11 wt.% cobalt concentrations were obtained with the co-sputtering technique assisted by balanced magnetron. XANES analysis does

produce the valence of $CoTi_2$ thin films grown by the co-sputtering technique. XANES analyses indicated Co^{2+} and Ti^{+}.On the other hand, the atomic positions of the first three first neighbors of the CoTi/Si samples were obtained by EXAFS experiments. The software package FEFF was used to determine the distances of the first neighbors and coordination numbers. FEFF found percentages of error in the range of 3.5–6.9% (see Table 1).

EXAFS is a technique for the analysis of structural parameters and, with the help of ab initio fittings, can be extended to provide very good structural information for a large number of materials, whether they be crystalline or amorphous.

Finally, we conclude that the main difficulty to produce CoTi2 thin film by using DC co-sputtering is the way to get the correct stoichiometry. The small Co wafers sometimes need be with same thickness and area. As a futures work will be try to increase the amount of CoTi2 phase with an improved the reproducibility.

Acknowledgements

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