Combined XPS and first principle study of metastable Mg–Ti thin films†

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X-ray photoelectron spectroscopy (XPS) was employed to investigate Mg80Ti20 thin film samples prepared by magnetron sputtering and density functional theory (DFT) calculations were performed on atomistic models with similar stoichiometry. As Ti is known to be immiscible in Mg, the microstructure and atomic distribution of Mg–Ti thin films are not fully understood. In this work, it was shown by DFT calculations that the density of states (DOS) depends strongly on whether Ti is arranged in nano-clusters or if it is distributed quasi-randomly. The calculated DOS was compared to valence band spectra measured by XPS, as a new way of indirectly probing short-range order of such thin films. The XPS results of Mg80Ti20 were found to correspond best with the DOS calculated for the nano-cluster model, supporting the view that Ti forms small clusters in such sputtered thin films. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Thin films composed of Mg–Ti with hydrogen exhibit interesting optical and electrical properties. Possible applications range from coatings on solar collectors and smart windows to optical hydrogen sensors and semiconductor devices. In order to utilize this potential, a detailed understanding of their electronic structure is important.

Ti is immiscible in Mg, but the two elements may be joined together by non-equilibrium synthesis procedures like magnetron sputtering of thin films. Since the material in such films often lack long-range order, it is difficult to identify their microstructure and local crystal structure with standard methods. Previous investigations of Mg–Ti–H thin films by Rutherford backscattering spectrometry, X-ray diffraction (XRD) and transmission-electron microscopy indicated the presence of a single phase in such films, in spite of the general tendency of Mg and Ti to phase separate. It was concluded that if Ti had segregated by precipitation from Mg–Ti solid solution, it must have formed small particles with sizes below the XRD detection limit. Evidence for such chemical short-range ordering was later found from simulations of optical isoethers obtained by the hydrogenography technique and further verified by a combination of XRD and extended X-ray absorption fine-structure spectroscopy. Density functional theory (DFT) calculations confirmed that the formation enthalpy per Ti atom was indeed lowered by up to ~0.5 eV when Ti was arranged in nano-clusters rather than distributed quasi-randomly.

As a continuation of our previous work, the present study compares calculated DOS to valence band spectra measured by X-ray photoelectron spectroscopy (XPS). This is a new way of indirectly probing the short-range order of sputtered thin films.

Methodology

200 nm thick Mg80Ti20 films covered with 1.5 nm of Pd were deposited in a UHV system (base pressure = 10−6 Pa) by DC/RF magnetron co-sputtering of Mg (99.95%) and Ti (99.999%) targets in 0.3 Pa of Ar, on single-crystal Si(100) substrates. The substrate was kept at room temperature. In order to obtain homogenous films the substrate was continuously rotated during sputtering. The typical deposition rate was 2.2 Å/s at 150 Watt RF for Mg and 0.42 Å/s at 131 Watt DC for Ti. A Pd (99.98%) caplayer of 1.5 nm was sputtered with a rate of 0.58 Å/s at 25 Watt DC to prevent oxidation.

The samples were investigated by XPS using a KRATOS AXIS ULTRA DLD instrument with monochromatic Al Kα radiation (hv=1486.6 eV) operated at 15 kV and 15 mA. The Pd layer was removed by sputtering an area of 2 mm x 2 mm with a 500-V Ar + ion beam delivering 100 μA of current. To minimise cratering effects and avoid detection of Pd, the measurements were done using a ‘small spot’ aperture with a 110-μm diameter. High-resolution spectra were acquired with pass energy 20 eV and dwell time 200 ms. To monitor the possible effect of oxidation during measurement, the data was collected in 10 consecutive scans of about 20 min each which were then added together to obtain the adequate signal-to-noise ratio. An increasing amount of MgO was observed, but the change in the valence spectrum did not seem to fundamentally alter the region which was compared to the calculated data as it occurred at a higher binding energy. Data processing was done using CasaXPS.

DFT calculations at the PBE-GGA level were performed for a Mg81.25Ti18.75 composition using the Vienna Ab-Initio Simulation...
The technical details can be found elsewhere. To obtain a composition and size comparable to the experimental sample, a 4x4x2 Mg unit cell was used, containing 64 atoms. Parallel calculations were performed for Ti distributed quasi-randomly and arranged in nano-clusters. In the quasi-random calculations, the Ti atoms were distributed in the cell at random, while the model of segregated Ti was constructed by using sheets of four Ti atoms stacked together in the a direction. Structural optimizations were performed using the standard hexagonal structure of Mg as a starting point. Volume, lattice parameters and atom positions were allowed to change simultaneously. For comparisons with the XPS spectrum the calculated DOS was scaled using photoionization cross sections from Yeh & Lindau.

Results and discussion

DFT calculations of the density of states (DOS) revealed significant differences for the two arrangements of Ti in Mg. In the quasi-random model, the calculated DOS had one dominant peak centred around the Fermi level, while the nano-cluster model gave two peaks, one on each side. Fig. 1 shows the total DOS for each model, along with total DOS for Mg and Ti separately. In both models, the dominant contribution to the total DOS is the Ti d orbital (not shown). Comparing the total DOS of Ti in the Mg–Ti mixture to the calculated DOS of pure Ti, it becomes clear that in the nano-cluster environment, Ti resembles elemental Ti, while in the quasi-random arrangement, the Ti DOS is significantly distorted. This corresponded well with our previous work where it was found to be energetically favourable for Ti to segregate into nano-clusters; which allowed it to simulate elemental state. The difference between quasi-random and nano-cluster is much less pronounced for Mg. The location of the valence peak compared to the Fermi level is related to the charge transfer between Mg and Ti: When Ti is distributed quasi-randomly, it attracts charge from Mg, which results in the peak centred at 0 eV. Ti in nano-clusters, however, forms Ti–Ti bonds which bind the electrons more tightly and results in a peak centred below 0 eV. In Fig. 2, the d states of three different compositions, Mg_{81.25}Ti_{18.75}, Mg_{93.75}Ti_{6.25} and Mg_{98.44}Ti_{1.56} are shown together with elemental Ti. The Mg_{98.4}Ti_{1.6} composition, with only one Ti atom in the 64 atom unit cell is totally without features. The Mg_{81.25}Ti_{18.75} composition, with 12 Ti atoms, resembles the elemental Ti, as already discussed. The Mg_{93.75}Ti_{6.25} composition, with 4 Ti atoms, has similar features, but is shifted about 0.5 eV towards higher energies. This demonstrates again that even for such small clusters, Ti is able to form states similar to those of pure bulk Ti. The difference between one Ti atom alone and just a few Ti atoms in a nano-cluster is pronounced.

The striking differences between the calculated DOS of the nano-cluster and quasi-random models encouraged a direct comparison between the calculated results and the XPS valence spectrum of a...
real sample. Even if it is well-known that DFT calculated spectra at this level of theory (GGA) generally are only qualitatively matching experimental data (errors can be in the eV range), this could be sufficient to distinguish important features in the experimental spectra. It should be noted that collecting such data from the Mg–Ti sample was not without practical challenges. The rapid oxidation of Mg and Ti required the deposition of a Pd capping layer, which had to be sputtered away in situ. Even in UHV, the sample oxidized during data acquisition. The experiment setup was aiming to minimise the effect of these obstacles as explained in the methodology section. Fig. 3 shows the Mg 2p and Ti 2p spectra. Both Mg and Ti were clearly detected in the sample, with some presence of oxide seen on the high binding energy side of the peaks. Fig. 4 shows the calculated results together with the XPS valence spectrum, which has a peak located at approximately −1 eV. The resolution of the experimental spectrum is much inferior to that of the calculated data due to instrumental effects. Moreover, the signal-to-noise ratio of the XPS data is limited by the acquisition time, and the inevitable presence of oxides will serve to broaden out single phase features of the valence band spectrum. Bearing these conditions in mind, the experimental data still seems to follow the DOS calculated for nano-clusters of Ti, rather than the quasi-random one. This is mainly manifested by the presence of a DOS maximum at −1 eV below the Fermi level in very close agreement with the experimental data. Obviously the XPS spectrum will only show states below the Fermi level, but for a peak located exactly at the Fermi level a steeper decline towards 0 eV should be expected.

Conclusions

In this work, DFT calculations showed that arranging Ti in nano-clusters within Mg leads to significant differences in the DOS as compared to Ti being distributed quasi-randomly in Mg. In both cases, the main contributor to the total DOS was the Ti d state. When Ti was allowed to segregate into nano-clusters in Mg, the Ti DOS started to resemble that of pure Ti, while in the quasi-random arrangement, the Ti DOS was severely distorted. The calculated DOS was compared to valence band spectra measured by XPS, as a way of investigating the microstructure of Mg–Ti thin films. The XPS results were found to correspond best to the DOS calculated for the nano-cluster model, further supporting the view that Ti forms small clusters in such sputtered thin films.

References