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“One-sample concept” micro-combinatory for high throughput TEM of binary films

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ABSTRACT

Phases of thin films may remarkably differ from that of bulk. Unlike to the comprehensive data files of Binary Phase Diagrams [1] available for bulk, complete phase maps for thin binary layers do not exist. This is due to both the diverse metastable, non-equilibrium or instable phases feasible in thin films and the required volume of characterization work with analytical techniques like TEM, SAED and EDS. The aim of the present work was to develop a method that remarkably facilitates the TEM study of the diverse binary phases of thin films, or the creation of phase maps. A micro-combinatorial method was worked out that enables both preparation and study of a gradient two-component film within a single TEM specimen. For a demonstration of the technique thin Mn_xAl_{1-x} binary samples with evolving concentration from $x=0$ to $x=1$ have been prepared so that the transition from pure Mn to pure Al covers a 1.5 mm long track within the 3 mm diameter TEM grid.

The proposed method enables the preparation and study of thin combinatorial samples including all feasible phases as a function of composition or other deposition parameters. Contrary to known “combinatorial chemistry”, in which a series of different samples are deposited in one run, and investigated, one at a time, the present micro-combinatorial method produces a single specimen condensing a complete library of a binary system that can be studied, efficiently, within a single TEM session. That provides extremely high throughput for TEM characterization of composition-dependent phases, exploration of new materials, or the construction of phase diagrams of binary films.

1. Introduction

Combinatorial techniques are very effective in the study of the correlations of preparation parameters, e.g. composition and physical properties of diverse materials. Combinatory is widely used in chemistry, biology and pharmaceutical innovation. In materials science, “multiple-sample concept” was suggested by Hanak in 1970 [2] who, instead of searching for new materials by studying only one composition at a time, proposed combinatorial solutions. The first examples for combinatorial preparation of samples for microscopy investigations were published in the 1990s and thence, the development of the field has a continuous interest. Schultz and co-workers [3] applied computer aided mask movement to prepare samples of various compositions at a density of 10,000 sample/in^2. Roskov et al. [4] used combinatorial technique to deposit polymer samples onto individual TEM grids, so that each sample exhibited different composition. Rack et al. [5] used DC magnetron sputtering from up to 4 targets to deposit combinatorial layers spread over a surface of several cm-size and applied a computer simulation to predict the film composition. Julthongpiput et al. [6] prepared a series of organosilane specimens with a gradual change from hydrophobic to hydrophilic and the samples were investigated by contact angle measurements, atomic force microscopy, and automated optical microscopy. Olk and Haddad [7] applied combinatorial deposition of 64 discrete samples from up to four sputtering targets to systematically control the microstructure of $Al_xSi_{(1-x)}$ alloys through variations in composition and growth temperature. The microstructure, surface morphology and phase distribution were investigated using X-ray diffraction and atomic force microscopy techniques.

Regarding efficiency, the above techniques represent partial solutions: the way of preparation is combinatorial, the investigation, however, has to be carried out on a number of individual samples, one at a time. Barna and co-workers [8, 9] applied an experimental arrangement in which a sample with variable composition was both deposited and investigated within a single TEM grid: A shield with a 1 mm diameter aperture was fixed above the grid so that a pair of evaporation sources was facing the substrate at different angles, through the aperture. As an alternative solution to aperture

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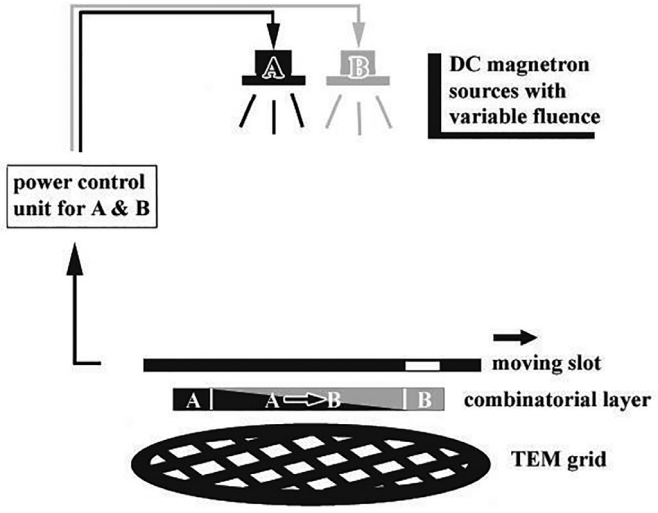

Fig. 1. Set-up for micro-combinatorial deposition. Components A and B are deposited by DC magnetron sputtering onto a TEM grid through a moving slot. The output powers of the sources "A" and "B" are adjusted in accordance with the position of the slot along the grid. The track of a thin micro-combinatorial layer is deposited in 3 sections: pure A, gradient section of A ⇨ B and pure B that are 0.5, 1.5 and 0.5 mm long, respectively.

a small platelet was fixed edge-on at the center of the TEM grid. As a result the grown films showed spatially varying composition at the area of half-shadow of the aperture, or of the platelet.

The method [8, 9] represents a "one-sample concept", however, suffers from fundamental flaws: (i) the concentration profile is unintentional (ii) the area of variable composition is very short, (iii) it does not cover the entire (0–100%) range and (iiii) poor reproducibility. These failures cause positioning of a wished composition go beyond control, inhibit both a clear separation of the various phases and a revelation of the whole set of data, therefore, impedes the method to spread.

The aim of the present work was to develop a one-sample technique that corrects the incompleteness of the above solutions. The so-called "micro-combinatory" (μ-combinatory) introduced in this paper is known to be the first that enables both preparation and investigation of a combinatorial binary specimen within a single TEM grid, that covers the entire (0–100%) composition range and exhibits a programmed concentration profile providing clear separation and easy positioning of the composition-dependent phases. Thanks to its all-in-one feature, such a μ-combinatorial sample enables a high throughput TEM study of a complete library of a binary system. For a demonstration of the method thin μ-combinatorial MnAl samples will be discussed here. MnAl is of recent technological interest [10] due to its tetragonal phase with hard magnetic properties.

2. Experimental

The principles of the preparation of a μ-combinatorial sample are as follows:

A_xB_{1-x} sample with gradient composition, in the range of $0 \le x \le 1$, is deposited along a track that fits a 3 mm diameter TEM grid. This is implemented by means of a device [11] that actuates a shutter with a 0.2×1 mm^2 slot in fine steps above the TEM grid meanwhile the powers of the two DC magnetron sources "A" and "B" are regulated in sync with the propagation of the slot: the fluence of component A gradually decreases from its 100% to 0%, and that of B changes inversely, from 0% to 100% (a dependence of the fluence on the output power was calibrated, previously, for both sources).

A typical sample appears as a 1 mm wide and 2.5 mm long layer track including a gradient section of 1.5 mm in length that is enclosed in between 0.5 mm long sections of exclusively A and B materials, respectively.

The arrangement for deposition and the build-up of the μ-combinatorial TEM specimen are illustrated in Fig. 1. The three sections of the layer track deposited on the grid are indicated in the scheme: A on the left and B on the right represent sections of 100% component A and 100% component B, respectively and in between them, A ⇨ B represents the gradient section. This built up of the sample makes possible the TEM characterization of both the binary phases of variable compositions and the phases of the constituting (A and B) materials.

The deposition of Mn–Al μ-combinatorial samples was carried out as follows:

The samples were deposited on TEM grids covered with either carbon, or SiO_x foil. The vacuum system was evacuated with a turbo molecular pump to a base pressure of 5×10^{-6} Pa. The grids were mounted in the μ-combinatorial device and load-locked into the chamber. Ar sputtering gas was introduced to the system at a partial pressure of 2.5×10^{-1} Pa. Both targets were cleaned behind closed shutters by pre-sputtering with their 100% power for 5 min. Based on previous calibrations the maximum (100%) power values for the Mn and Al sources were selected to be 225 W and 150 W, respectively that provided equal fluencies. Subsequently, the motion of the slot of the μ-combinatorial device was started (and maintained during the experiment), the shutter of the Mn source was opened and Mn was deposited through the moving slot onto the TEM grid. This provided the pure Mn section of the combinatorial layer track. In due time the power of the Al source was reduced to zero and its shutter was opened. It was followed by the gradual increase of the power of the Al source from 0 to 100%, simultaneously, with the decrease of the power of the Mn source from 100 to 0% and as a result the bimetallic, gradient section of the track was deposited. As the power of the Mn source arrived to zero and, simultaneously, that of the Al source arrived to its maximum, the Mn source was switched off and the pure Al section of the track was deposited. Finally, the shutter of Al source was closed, the source was switched off and the actuation of the slot was halted.

In order to prevent Mn-containing samples for oxidation a topping layer of amorphous Si-oxide was used that protected the sample for a remarkably long period, as well, during annealing [12].

The μ-combinatorial samples, prepared as above, were characterized by a 200 kV Philips CM 20 TEM and a 300 kV JEOL 3010 HREM. For a clear positioning within the sample the combinatorial layer track was aligned with the x-axis of the stage of the TEM. The local composition along the track was measured by a Bruker QX 200 Energy Dispersive X-ray Spectrometer (EDS) attached to the TEM, under conditions of elevation angle: 13°, sample tilting angle: 20° and measured area: ~5 μm diameter. For quantification standardless analysis by the Cliff–Lorimer calculation was applied using the Al Kα and Mn Kα peaks with the sensitivity factors $k_{Al} = 0.985$ and $k_{Mn} = 1.350$. The structure and morphology was investigated by bright and dark field imaging and selected area electron diffraction (SAED). The evaluation of the SAED patterns was carried out with the help of the software "Process Diffraction" developed by Lábár [13]. It is to mention that only the peak positions of the Pdf database were used for identification of phases, the aspects of peak intensities were not considered.

3. Results and discussion

The photo of a TEM grid with a Mn–Al μ-combinatorial sample DC sputter-deposited onto carbon foil by the method described above is shown in Fig. 2. The dimensions (2.5×1 mm^2) of the