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**Scanning X-Ray Diffraction: A Technique with High Compositional
Resolution for Studying Phase Formation in Co-Deposited Thin Films***

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SCANNING X-RAY DIFFRACTION: A TECHNIQUE WITH HIGH COMPOSITIONAL RESOLUTION FOR STUDYING PHASE FORMATION IN CO-DEPOSITED THIN FILMS.

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ABSTRACT

Investigation of the formation of new metastable phases in alloy thin films requires ways of quickly determining the crystalline structure of samples with different compositions. We report a novel technique for acquiring structural information from films intentionally grown with a composition gradient. For example, binary metal alloy films were deposited using a phase-spread sputtering method. In this way essentially the entire composition range could be grown in a single deposition. By using a narrow incident x-ray beam and a translating sample stage combined with a position sensitive x-ray detector technique, detailed information of the metastable phase diagram can be obtained rapidly. Compositional resolution of the order of $\pm 0.2\%$ can be achieved, and is limited by the brightness of the x-ray source. Initial results from studies of phase formation in Zr-Ta alloys will be presented. Extensions of the analysis technique to ternary systems will be discussed.

INTRODUCTION

Even for binary systems, where virtually every compound has been studied and equilibrium phase diagrams established, there remain systems in which extended solubility, metastable-, and amorphous phase formation are unexplored. The development of material for use in, e.g., corrosive, and oxidizing environments requires that many alloy systems be investigated in detail. This task usually requires fabrication of a large number of samples with varying chemical composition, and subsequent application of analysis techniques. There is no conceivable way out of this dilemma if solely bulk specimens are considered.

Thin film co-evaporation, on the other hand, has proven versatile since films of different compositions can be simply fabricated by altering the relative deposition rates. Films themselves are used as protecting coatings and diffusion barriers but can, under adequate deposition conditions, be used as model systems for later bulk sample fabrication.¹ A feasible approach to rapidly obtain samples covering large portions of composition space is to use relatively large substrates, and the spread that occurs due to spatially separated deposition sources. The microstructure of the obtained films and the degree of metastability in the films can be varied by appropriately choosing deposition conditions, such as substrate temperature.

Once a quick sample manufacturing process exists, characterization limits fast surveying of the phase space. This becomes even more pronounced when the phase spread geometry is utilized. For example, the study of phase formation performed using XRD is a task that becomes rather tedious if high compositional resolution is required. In this paper a new technique, Scanning X-Ray Diffraction (SXRD) is described. It significantly reduces analysis times needed to acquire structural information connecting chemical composition with occurrence of various phases. The Ta-Zr binary system was chosen as a model for metastable phase diagram studies.

FILM DEPOSITION

The films were grown in a dual triode sputtering gun system, as illustrated in Fig. 1. The two guns were located next to one another. The target material was 12 mm diameter and 6 mm thick metal disks, bonded to a water cooled copper backing plate. The high vacuum chamber was cryogenically pumped with additional pumping provided by a titanium sublimation pump. Consequently, no pumping oils were in contact with this system, which was rough pumped using a dry rotary vane pump. The base pressure was better than 6×10^{-6} Pa.

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Sputtering was performed using 10 mTorr Ar introduced through the guns, close to the target surfaces. Target voltages of 200-400 V were used, resulting in sputtering powers of 30-60 W, per gun. Oscillating quartz sensors were used to monitor the deposition rates, which were in the order of $2\text{-}3 \text{ \AA s}^{-1}$.

The substrates were r-cut sapphire wafers mounted on a stainless steel heater block. The block was heated using a resistive element and the temperature was controlled with a thermocouple located within the block. The substrate size was 12 mm wide by 95 mm long, and held at a distance of 40 mm from the target surfaces. The arrangement is shown to scale in Fig. 1.

Fig. 1. Schematic drawing of the vacuum deposition chamber, displaying a side view of the phase spread geometry.

Fig. 2. Ta content x as a function of position on the substrate. Arrows indicate the locations of Zr and Ta target centers, respectively.

FILM ANALYSIS AND SCANNING X-RAY DIFFRACTION (SXRD)

X-ray fluorescence (XRF), and Rutherford Backscattering Spectroscopy (RBS) were used to obtain the composition as a function of position. Such a graph is shown for Zr-Ta alloy films in Fig. 2. The positions of the Zr and Ta target centers are indicated. Data points obtained by both RBS and XRF represent averages over app. $2 \times 2 \text{ mm}^2$ regions. By interpolation a calibration curve of composition vs. substrate position can be drawn. For films grown at varying temperatures analysis repeatedly showed that the composition varied reproducibly and smoothly from one wafer to the adjacent ones.

For structural analysis a rotating Cu anode X-ray diffractometer was used. Variable slits were placed in the incident beam in order to restrict the analyzed specimen area to a narrow line perpendicular to the composition gradient, see Fig. 3. The diffracted beam was monochromatized and reflected out of the plane by a flat graphite analyzer crystal and detected in a position sensitive detector (PSD). The technique has been described in detail elsewhere,² and allows for simultaneous acquisition over approximately 5 degree range in 2θ . Ti-W-N and polycrystalline alumina samples were used to experimentally assess the acquisition efficiency and spatial resolution, respectively. Compared to a standard powder diffractometer, employing the Bragg-Brentano geometry (BB), it offers significantly faster data collection. This is evident in Fig. 4 where PSD and BB methods are compared. The scan speed was 2.5 times faster and the signal to noise ratio 10 times better in the PSD case. Taking these facts and x-ray intensity factors into account a 50-fold enhancement in efficiency was achieved.

Fig. 3 A schematic illustration of the SXRD setup.

Fig. 4. Powder diffractograms showing the (002) peak of a Ti-W-N film, comparing the PSD diffractometer to the standard BB method.

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In order to survey the phase spread film a means of moving the sample in the direction of the composition gradient was required. Scanning was accomplished by mounting the specimens on a translating sample stage, as indicated in Fig. 3. There is a trade-off between short acquisition times for each diffractogram and the spatial resolution, which both depend on the slit width. With this x-ray source acceptable count rates were achieved for widths down to 0.1 mm, which corresponds to a beam width W_0 less than 0.2 mm at the sample location. The actual spatial resolution W is, however, dependent on the diffraction angle. In Fig. 5 several diffractograms showing the alumina (116) peak at $2\theta = 57.5^\circ$ are shown. The scans were acquired at different positions measured relative to the alumina wafer edge and the intensity actually drops to zero over a distance of less than 0.4 mm.

Application of the SXRD method is now demonstrated by effectively mapping the metastable phase diagram of Ta-Zr. Fig. 6 shows SXRD results obtained from a film quenched from vapor to a substrate held at 250°C . Shown here is a transition between two crystalline states, one Zr rich and the other Ta rich. In order to show this as clearly as possible only a limited range of diffraction angles are shown here. From a full analysis, however, we have concluded that the two crystalline peaks correspond to metastable bcc solid solutions with unit cell sizes 3.55 and 3.36 Å, respectively. The incipient phase in-between shows no other diffraction than the broad feature shown in Fig. 6, and might be an amorphous phase. In the Ta rich end of the phase spread, shown graphically in Fig. 7, a peak assigned to (002) $\beta\text{-Ta}^3$ occurs at $2\theta = 33.7^\circ$ in a very narrow range of $0.98 < x < 0.99$. The film is two-phase in this region, the other phase being bcc Ta with a unit cell size of 3.32 Å, which is close to the bulk Ta value.

Fig. 5. A sequence of diffractograms showing the (116) peak of an alumina wafer. The sample position is given relative to the wafer edge.

Fig. 6. SXRD obtained from a $Zr_{1-x}Ta_x$ film grown at 250 °C.

SUMMARY

The described phase spread growth technique is useful not only as a means of quickly obtaining a large number of samples. More importantly, since the relative rates vary smoothly, all compositions are covered continuously thus facilitating, for instance, determination of solubility limits and detection of intermediate phases. Accurate chemical analysis of the phase spread films is necessary to obtain the desired correlation between structure and composition.

To take full advantage of the rapid sample fabrication method, a means of fast structural characterization is essential. We have here reported of the SXRD-technique which is based on obtaining several consecutive diffractograms from different areas (compositions) of the sample. For reasonable analyzing times the spatial resolution is better than 0.4 mm at 57.5° diffraction angle. This may be converted to a compositional resolution which is dependent on the actual composition gradient, c.f. Fig. 2, but is in the present experiment on the average $\pm 0.2\%$ absolute. The resolution could be improved either by reducing the composition gradient, i.e., use larger substrates, or by utilizing brighter x-ray sources, like synchrotrons. In such an experiment it would also be possible to analyze small spots on two-dimensional phase spreads in studies of phase formation in ternary systems.

Figures 6 and 7 illustrate examples of the versatility of SXRD in investigating phase formation in binary alloy systems. In the first case the possibly amorphous transition range between two metastable bcc structures was determined and in the second case the occurrence of non-equilibrium or impurity stabilized β -Ta was shown in a narrow composition range. At this point it should be pointed out, however, that once the interesting regions of the phase spread have been discovered, final phase identification and microstructural characterization should be undertaken, using, e.g., electron microscopy.

Fig. 7. Pseudo 3D graph showing SXRD from the same $Zr_{1-x}Ta_x$ film as in Fig. 6, in this case displaying the Ta-rich end of the phase spread.

In the present experiment the composition as a function of position on the substrate was determined in a separate system. A highly desirable further improvement of the technique should include the capability of simultaneous composition and diffraction analysis.

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