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Applications Note

Group Array Analysis of a Combinatorial Thin Film System

MO455(A)

Keywords group array analysis, ESCApe, thin film materials

Overview

The last few decades have seen rapid development in computational and theoretical tools for fabricating, simulating, and characterizing material systems. In this applications note the potential of surface characterization by X-ray photoelectron spectroscopy to provide rapid elemental and chemical state information is presented. The development of the group analysis array functionality is of significant importance in the application of XPS analysis to combinatorial materials discovery to allow the processing and display of large data sets. As will be demonstrated, group array analysis provides a more detailed understanding of the chemical distribution across the sample.

Introduction

Surface characterization of film depositions is often performed by analyzing only a limited number of points, with the results assumed to be representative of the deposited chemistry. In analyzing data and displaying results, the analyst is often limited to calculating data from the selected points and generating a table with some measure of statistical comparison. Compositional mapping is central to obtaining comprehensive pictures of material systems and mapping active chemical properties such as oxidation state and alloying as a function of composition. This is an integral part of understanding the underlying physical and chemical properties of the material. The development of software to handle large matrices of analysis locations, coupled with group analysis of the results offers a more comprehensive approach to determining the homogeneity of the deposition and identifying regions of differing composition.

The combinatorial approach has been widely used to discover new material phases for many years now, allowing rapid exploration of compositional and structural properties in complex material systems. Here the traditional approach of combinatorial techniques to explore several model systems using X-ray photoelectron spectroscopy (XPS) is coupled with the group analysis array functionality to paint a comprehensive picture of the surface structure of the deposition results.

Experimental

A ternary shape memory alloy, NiTiCo, was deposited across a 3” wafer by UHV magnetron sputtering of high purity Ni, Ti and Co targets at room temperature. The resulting thin film was annealed in Ar at 500 °C for 1 hour, an important step in ensuring film homogeneity. NiTiNOL is a well known shape memory effect (SME) material. Importantly, Co is known to reduce the transformation start temperature and

range which is an important consideration for medical and ambient temperature applications. For this sample the aim was to incorporate 1—3 % Co.

The surface elemental distribution of the deposited system was initially evaluated with XPS wide energy range, survey scans. Local chemical bonding is investigated using high resolution acquisition to identify regions of interest for additional analyses, including depth profiling of the structure to determine the layering nature of the resulting chemical states formed during the deposition.

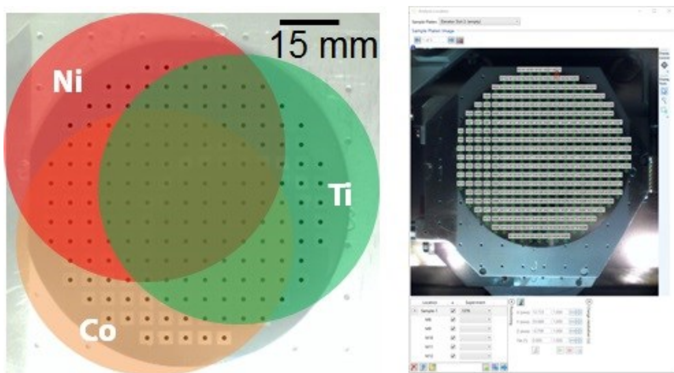

Figure 1: (Left) geometry of the sputter deposition targets relative to the 3" wafer substrate. (Right) discrete array analysis positions defined in the ESCApe software.

The group array analysis functionality of the ESCApe software allows easy definition of an array of analysis points across the sample. In this example, 177 discrete positions were defined as equally spaced points across the wafer. The positional information of each spectrum was retained so that spectra were linked by Cartesian coordinates, greatly easing subsequent data handling and analysis of elemental distribution. Group analysis is used to generate an overall elemental compositional distribution profile, and similar group analysis is used to explore the different chemical bonding and oxidation states on the surface of the film.

Al Kα excited 60 second survey spectra were acquired at each position such that the entire data collection was achieved in 3 hours. To facilitate the data processing, the ESCApe software has an automated peak identification capability which can be extended to define a background around the core level transition which results in a quantified survey spectrum. This is propagated across all 177 spectra so that elemental quantification is achieved in a matter of minutes.

Where sub-surface alloy composition was required, sputter profiles were performed using 2 keV Ar^+ ions with a 2x2 mm etch crater. The etch cycles were repeated until a steady-state elemental composition was measured.

Results and Discussion

The elemental concentration determined from the survey spectra may then be plotted as a function of position as shown in Figure 2. It is immediately apparent that the elemental con-

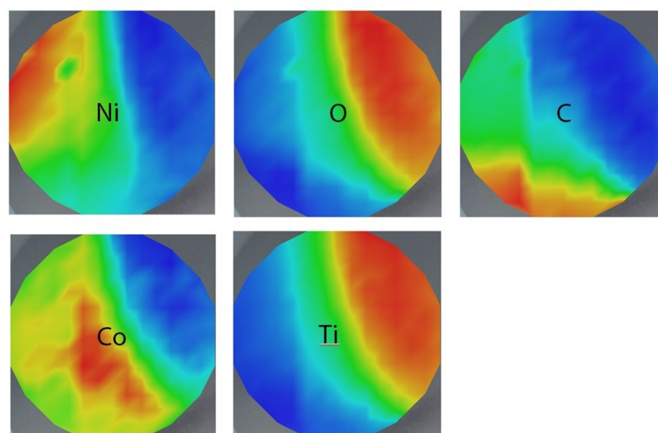

Figure 2: Elemental concentration as a function of position where the 'hotter' colours indicate higher concentration.

centration varies across the surface, with the highest concentrations for each element being adjacent to the sputter target position. To demonstrate the greater information that can be extracted from the array dataset the Ni distribution and chemistry was investigated. Figure 3a shows the Ni $2p_{3/2}$ region summed from all 177 spectra with a model fit. The red component at 850.2 eV binding energy is assigned to Ni in the metallic state alloyed with Co/Ti. The blue components are assigned to Ni^{2+} which is most likely to be nickel hydroxide as evidenced by the distinctive shake-up structure above the photoemission peak at 854.0 eV. The model shown in Figure 3a was propagated across all the spectra and the concentration of each chemical state plotted as a colour map across the wafer, shown in Figure 3b.

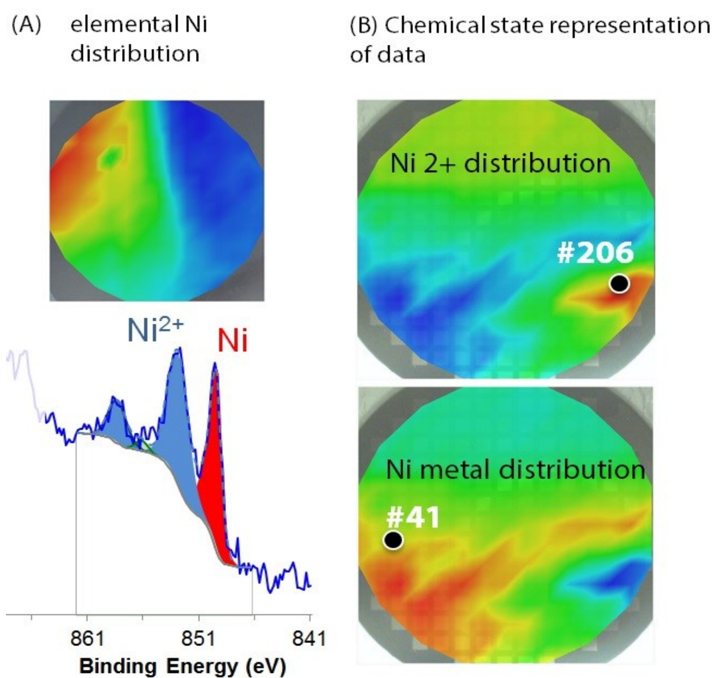

Figure 3(a) Elemental distribution of the Ni and summed Ni $2p_{3/2}$ region with model fit for metallic and Ni^{2+} oxidation state. (b) Chemical state distribution of the two Ni chemical states.

To understand the sub-surface alloy composition, two positions were chosen to perform a sputter depth profiles. This allowed the determination of the alloy composition after removal of the adsorbed carbon surface contamination. The profile was continued until a steady state elemental composition was reached. Figure 4 shows the depth profiles from these two analysis positions, #76 and #218.

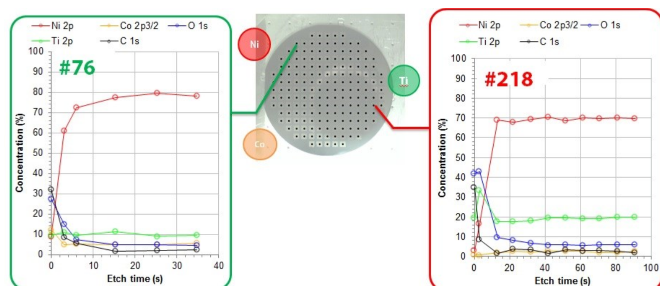

Figure 4: 2 keV Ar^+ sputter depth profiles into the bulk alloy material at points #76 and #218.

From the depth profiles it is shown that the surface adsorbed carbon, which is 35-40 rel.at.% of the surface composition, is removed after the first 2 or 3 etch cycles. It is noted that the carbon is not completely removed, which prompts further investigation which is detailed below. It is also shown that in the Ti rich region associated with position #218, there is an increase in the surface concentration of Ti which implies some surface segregation of the Ti during the alloying process.

To gain further insight into the carbon chemistry, both across the surface of the wafer and the bulk of the material, a sputter depth profile was performed at a position adjacent to #218 (detailed above where surface segregation of the Ti was observed). During the profile a high resolution C 1s spectrum was also acquired allowing determination of the chemistry into the bulk of the material. The depth profile and high resolution C 1s region are displayed in Figure 5.

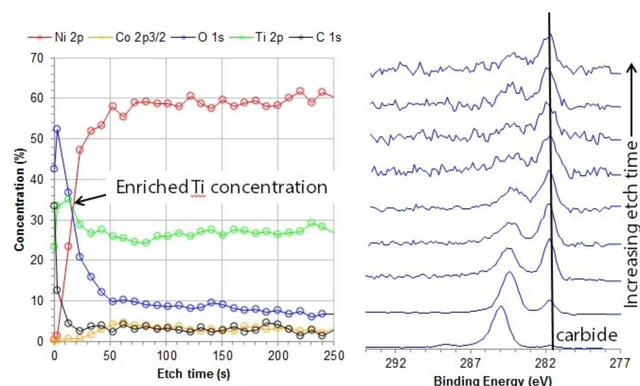

Figure 5: Sputter depth profile through position #207 with the C 1s narrow region spectra acquired during the profile.

The high resolution C 1s spectra show that the adventitious hydrocarbon envelope, between 285.0 eV and 287.5 eV, is removed after 4 etch cycles. However, the carbide peak persists into the bulk of the material. Under the typical high vacuum growth conditions used in this work, several sources of C are possible, with two perhaps most obvious choices being residual gas molecules and target contaminants. Dissociation of residual C=O molecules upon contact with the surface can be expected based on the results of ab initio studies performed for the CO_2/TiAlN system. In addition, C=O can dissociate upon electron impact in low pressure discharge (bond dissociation energy is 11.2 eV) constituting an alternative source of free carbon.[1] Moreover, the apparently low level of target contaminants specified by the vendors (here < 0.1 %), can be misleading as light elements like C are preferably sputtered along the target normal, so their content in the film might be significantly higher than in the target. Since both the background system pressure and the target purity level used in this work are typical for industrial processing it is reasonable to assume that the unintentional carbide formation reported here also takes place for other industrially-grown functional coatings with an affinity for carbon.

Lateral distribution of the carbon species was determined by fitting a model to the C 1s envelope for the adventitious hydrocarbon and the carbide species. Representative spectra for these carbon containing species are shown in Figure 6, along with the lateral distribution of the carbide material across the wafer.

Further investigation of the thin film chemistry was undertaken by measuring the Ti 2p high resolution spectra using the array acquisition method. In Figure 7(A), representative Ti 2p spectra from 2 discrete positions are shown. A model was created to fit the envelope with components corresponding to Ti-carbide, metallic Ti, Ti^{3+} and Ti^{4+} (TiO_2). This model was fitted to all 177 spectra and the distribution of each chemical state plotted as a function of position, as shown in Figure 7(B).

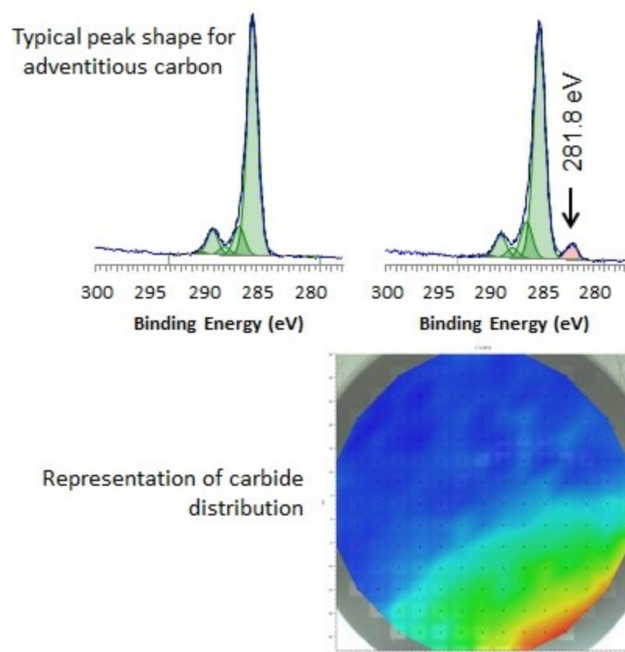

Figure 6: High resolution C 1s spectra from areas showing only adventitious hydrocarbon and adventitious hydrocarbon with carbide. Also shown is the carbide distribution across the wafer.

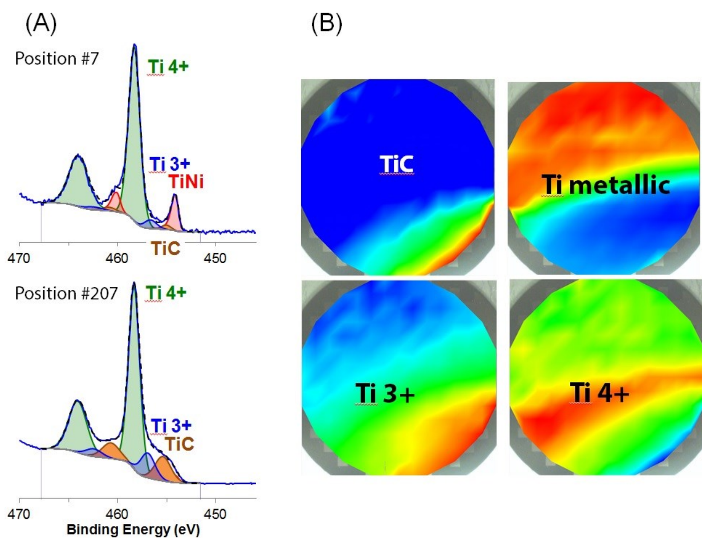

Figure 7(A): Representative Ti 2p high resolution spectra taken from positions #7 and #207, respectively, with a model fitted to account for Ti chemical states. (B) Distribution of Ti chemistry identified in (A).

It is immediately apparent that distribution of the TiC concentration is coincident with the carbide functionality identified in the C 1s spectra and plotted as a function of position in Figure 6. It is noted that the material properties of the thin film depend on the composition and since the initial search for viable shape memory alloy compositions is screening rapidly through many combinatorial thin films, it is important to know both the precise synthesis conditions for reproducibility and impact of the synthesis conditions. If the carbide has any influence on the material properties and steps are taken to limit carbon as a contaminant, then it is important to understand how to modify the synthesis procedure accordingly.

Conclusions

The development of the group array analysis acquisition and processing software provides much more intelligent use of large amounts of data. This in turn allows greater insight into the deposited thin film and facilitates the combinatorial approach to material research and development. This example demonstrates that a workflow where peak identification, background subtraction and subsequent quantification may be automated and no longer considered a rate limiting step in working with large amounts of data. Furthermore the suitability of XPS as a precise and fast technique for materials characterisation has been demonstrated.

Acknowledgements

We would like to acknowledge Naila al-Hasan and Ichiro Takeuchi from the University of Maryland for the thin film sample and helpful discussion in interpretation of results.

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