Group Surface Chemical Analysis of Combinatorial Film Systems

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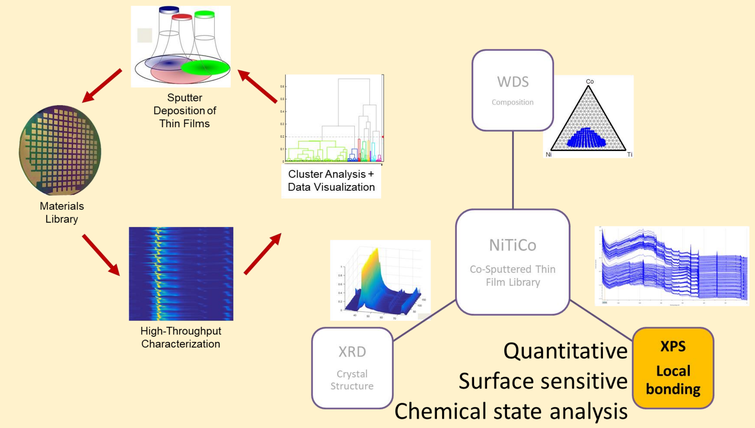
KRATOS ANALYTICAL A SHIMADZU GROUP COMPANY — 50 YEARS — Fifty Years of **XPS**

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 results 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 is an integral part of understanding the underlying physical and chemical mechanism of the properties. 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.

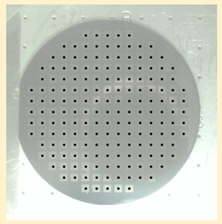
The combinatorial approach has been used widely to discover new material phases for many years now, allowing rapid exploration of composition–structure properties in complex material systems[1]. Here we will apply the traditional approach of combinatorial techniques to explore several model systems using X-ray photoelectron spectroscopy (XPS), coupled with group analysis of the results to paint a comprehensive picture of the surface structure of the deposition results.

ROLE OF XPS IN NOVEL ALLOY DEVELOPMENT

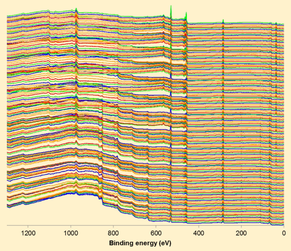


GROUP ANALYSIS

Sampling just three points from random locations on a specimen, as often specified in surface analysis requests, is not generally truly representative of a sample surface. Group analysis offers a more comprehensive analysis of the whole surface, illuminating inhomogeneous distributions and chemistries.



Optical image of the segmented wafer



60s fast acquisition spectra acquired across the wafer positions

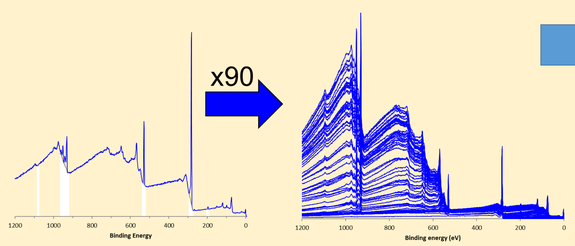
Application of Group Analysis to Reveal Chemical State Differences

The ternary shape memory alloy NiTiCo was deposited across a wafer and the geometrical deposition relationships investigated with multiple techniques, including XPS for the surface chemical analysis. The surface elemental distribution of the deposited system is evaluated with XPS wide energy scans, while the 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 in the deposition. Group analysis is used to generate a general 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. These group analyses reveal detail of the range of chemical states, including unexpected chemistries formed in the deposition process.

Group Analysis

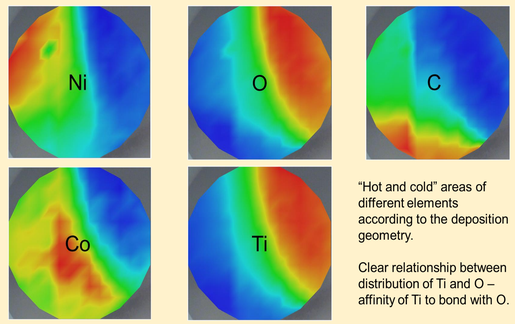
Ideally suited for investigating inhomogeneous distributions in combinatorial and patterned depositions.

INHOMOGENEOUS SAMPLES – WORKFLOW



Peak ID → Fit background → Propagate fitted background across dataset → Check for consistency

BACKGROUND SUBTRACTION, QUANTIFICATION.



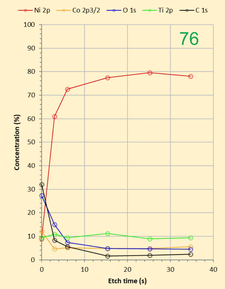
"Hot and cold" areas of different elements according to the deposition geometry.

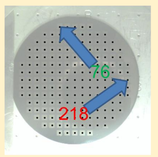
Clear relationship between distribution of Ti and O – affinity of Ti to bond with O.

Basic elemental quantification from wide range scans shows the level of compositional changes across the sample surface. This distribution information allows for some direct assessment, as well as identifying positions for additional analysis, such as depth profiling to reveal how the elements, and potentially chemical species, are vertically distributed. For this combinatorial deposited alloy system, elemental distributions indicate two generally separated regions. Points were then chosen for additional depth profiling, which revealed differing alloy compositions into the bulk, with 50% less titanium incorporated in comparison.

Higher resolution acquisition allows extraction of chemical state distributions across the surface, adding information to the elemental distribution obtained with the use of the initial survey scans. This allows even more detailed analysis of the chemical relationships and more specifics in the quantitative analysis. In this case, specific oxidation states of Ni were readily differentiated across the sample surface, and analysis of the high resolution carbon spectra from the group analysis showed a peak likely associate with carbide formation, with was then associated with the formation of titanium carbide in a small region of the surface. Choosing a point from this region, additional sputter depth profiling shows this carbide species to persist with depth into this region of the sample.

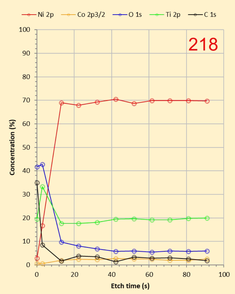
Focussed 2 keV Ar^+ ions used to remove uppermost atomic layers – more accurate determination of bulk stoichiometry.



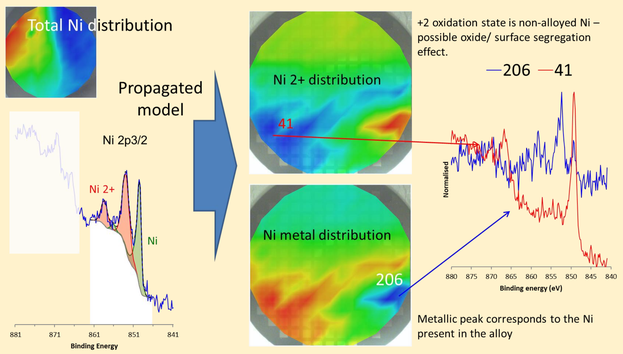


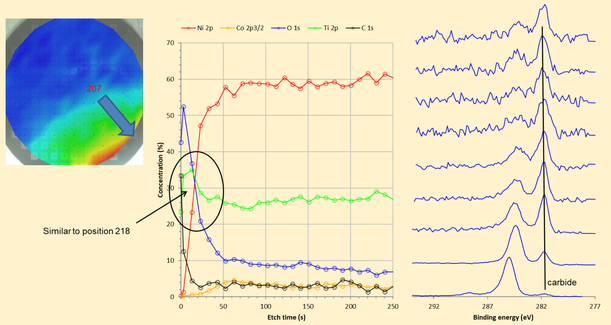
Much higher C content on areas of high Ni (low Ti)

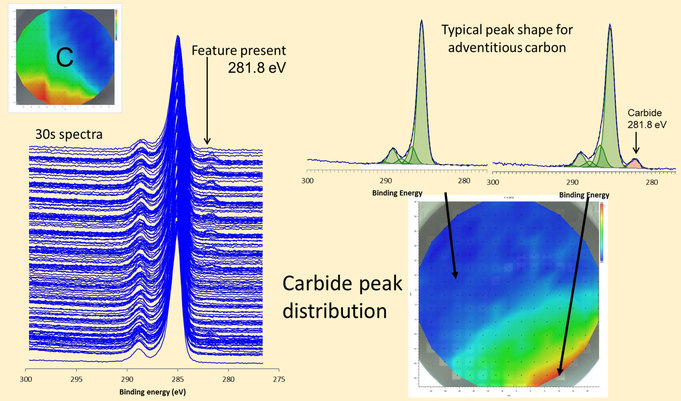
Removal of top C_{ad} results in higher Ti surface content which decreases to a steady state of ~20 at.%

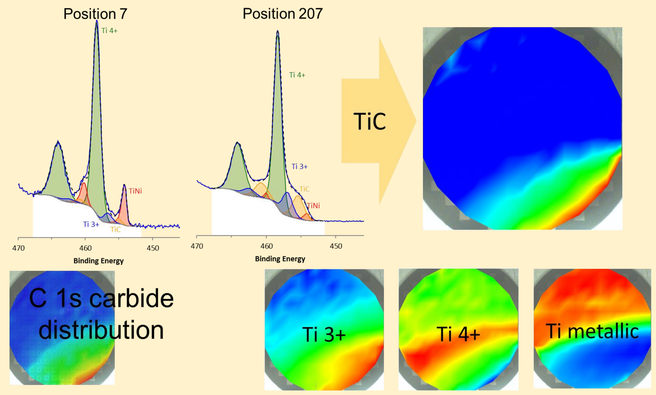


HIGH RESOLUTION (CHEMICAL STATE) IMAGES









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CONCLUSION

Group analysis allows for a more detailed understanding of the chemical distribution across a sample surface. The process maintains the spatial relationship between results, allowing the summary distributions to be visually displayed, and the data additionally investigated by drilling down to spectra at a location of interest. This can be applied to development of multi-element distributions, as well as allow for characterization of depositions or treatments intended to be homogeneous.