MATERIALS CHARACTERIZATION WITH 3-DIMENSIONAL ION MICROSCOPY/MICROPROBE ANALYSIS

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Abstract - An automated camera based detection system and image analysis system is described for secondary ion microscopy/ion microprobe analysis with the CAMECA ims 4f instrument. Procedures for high dynamic range image acquisition and display in the ion microscope operation mode rely on a single microchannel plate, a high sensitivity camera and a KONTRON IBAS image processor system. In the ion microprobe mode modifications are made to the primary deflection electronics of the SIMS instrument.

keywords : surface analysis, microscopical analysis, secondary ion mass spectrometry

In secondary ion mass spectrometry (SIMS) the surface of a sample is bombarded with a focused beam of energetic primary ions. The sputter process that takes place at the surface causes positive and negative secondary ions to be ejected from the outermost surface layers. These ions provide information on the composition of the surface layer upon mass analysis and collection.

In imaging SIMS instruments the secondary ion optics are designed so that the mass filtered secondary ion beam is projected in a way allowing the visualisation of the lateral distribution with combinations of microchannel plate/fluorescent screen (MCP/FS) and sensitive cameras [1-4]. In some configurations [e.g. 5] the MCP/FS is replaced with a charge coupled device (CCD) slow scan camera system. An alternative to the camera based detection systems for image acquisition relies on position sensitive pulse counting system using a resistive anode encoder (RAE) detector [6]. Sequential ion images as material is sputtered away from the sample surface provides depth profiles and three dimensional information.

In an alternative microprobe mode of exploitation of the instrument a focused primary ion beam is scanned over part of the sample surface with simultaneous pixel-by-pixel registration of the secondary ion current. Imaging SIMS with the microscope is limited to a lateral resolution of ca. 1 μm whereas the ion microprobe depends on primary ion beam size and extends lateral resolution well into the submicron range.

By combining these two modes of operation with image processing technology a method emerges that is capable of truly visualising the chemical composition of objects in 2 and 3 dimensions [e.g. 4,5]. To accomplish this for our instrument it was interfaced with a KONTRON IBAS image processing system. In the ion microscopy mode of utilisation a high sensitivity video camera is used for registration of the ion images. By using real time image integration this system allows visualisation of sub ppm impurities with typically analyzed areas of 250x250 μm^2 with a resolution of ca. 1 μm . For the ion microprobe mode substantial modifications were made to the primary beam deflection electronics of the CAMECA instrument. With the ion microprobe technique the lateral resolution in principle is only limited by the size of the primary beam (100-200 nm in our instrument, below 50 nm with other liquid metal ion sources)

Using image processing methods it becomes possible to obtain images showing the true elemental composition at the pixel level and to perform retro-depth profiling on freely selected features of the analyzed surface. Ultimately a 3 dimensional presentation of chemical composition at the interior of the object can be reconstructed from the measured stack of images obtained by successive sputtering and removal of material from the surface.

EXPERIMENTAL

The CAMECA 4f instrument used in this work uses mass filtered primary ions, O_2^+ , Ar^+ , or O^- produced by a duoplasmatron source or Cs^+ from a surface ionization source. The secondary ion system consists of an immersion lens and transfer optics, an electrostatic sector and a magnetic mass filter. The mass filtered secondary ions are registered on a MCP/FS assembly to visualise the ion image, which is viewed with a high-sensitivity (10^{-4} lx) MTI-66 silicon intensified target (SIT) camera coupled to the microscope with standard 50 mm or 28 mm lenses. The main functions of the mass spectrometer are controlled by a HP 9836 computer using HP-BASIC. A KONTRON IBAS system is used for image processing. It consists of the following components (see Fig. 1) :

Figure 1 : Schematic of the KONTRON IBAS image processor

Ion microscopy. The entire system can be operated in three different ways for ion microscopy :

- both SIMS and image processor used independently (e.g. for post processing of prerecorded images);
- with the image processor acquiring images from the SIMS experiment while both are working independently under the control of the operator;
- the image processor acts as a slave of the SIMS control computer with a connection between the HP computer and the image processor via a RS-232 serial interface.

The BASIC program controlling the SIMS computer in its standard configuration was modified to allow commands to the image processor and to communicate data such as identification tags and measurement parameters (e.g. mass being recorded, total ion current monitored...) To acquire reliable ion images the following parameters must be considered :

- (i) amplification of the microchannel plate and camera;
- (ii) the frame integration;
- (iii) matching of the dynamic range of the mass spectrometer with that of the image acquisition system.

(i) an AT personal computer under MS-DOS that controls the acquisition, processing and storage of images using functions selected from menus or using a C-like programmed mode;

(ii) an image processing unit consisting of several components, the video I/O board (VIOB) with video ADC and frame grabber, the real time video board (RTV) for on-line processing of the images (averaging, integration and masking operations executed at video rate) an image memory containing 8 Mbyte of image memory (expandable to 128 Mbyte), a microprogrammable image array processor (MIAP) for image processing and the memory address controller (MAC);

(iii) the slow scan interface (SEMBOX) allowing control of the primary ion beam in a programmable way.

In the system used, camera gain and high voltage of the intensifier are set automatically while the black level is set manually so that the black output of the camera corresponds with a minimum grey value in the image. The instrument was modified so that the high voltage of the microchannel plate is brought under control of the HP computer. When a first image of a given mass is acquired, the high voltage is set at its minimum position and the maximum grey level in the image is determined. Measurements are repeated at incrementally higher voltages until overflow is observed. In sequential image registration e.g. during sputtering for depth profiling analysis only a limited part of the search needs to be repeated for the optimization of the high voltage in order to account for ion current variation as a function of depth. In order to relate the grey level values to ion intensities, the total secondary ion current is measured with the electron multiplier or the Faraday cup and stored together with the image information.

A major limitation of the system is the dynamic range of the 8-bit deep image digitizer limiting the information in one image to 256 distinct grey levels (in practice to about 200). This is totally inappropriate for the high dynamic range SIMS information which varies in principle from very low concentrations (single ion counting) to imaging of matrix ions (10^9 ions per second). The dynamic range within an image is basically determined by the lateral variation in concentration within the field of view. To visualise large differences in intensity (or concentration) e.g. a local impurity at high concentration within a nearly homogeneous concentration level at trace concentration procedures must be developed to translate the information in the images in the 256 grey levels. By appropriate integration procedures it is possible to extend the dynamic range appreciably.

The real time capabilities of the VIOB allow the integration of up to 256 frames in a 16 bit RTV memory, thus reducing random noise in low intensity images. After an integration cycle of 256 frames the 8 most significant bits are retained and the 8 least significant bits (which contain most of the noise) are discarded.

By integrating successive integration cycles (of 256 frames) and transferring the pixels above a given grey level in a separate image while weak features become visible, high dynamic range images can be reconstructed. Using 5 recorded images a final image showing the log ion intensity with a dynamic range up to 20,000 is possible. The procedure is termed extended dynamic range imaging (EDRIM) and is more fully documented elsewhere [5].

Reconstructed depth profiling. The depth profiling program of the SIMS HP computer was modified to allow commands being given by the image processor via an RS-232 interface. During the successive mass scans the microchannel plate high voltage is optimised as explained earlier. A typical image size of 256x256 is stored for ca. 300 images consisting of 5 to 10 separate masses. The time required for such a three dimensional analysis is about 1 hour. The data occupy 20 Mbyte of hard disk memory space. The primary beam is interrupted when during acquisition the image memory is transferred to the hard disk. After acquisition a number of reconstructions are possible on the recorded data :

(i) conversion of the grey level of each pixel to ion current by scaling with a factor given as the total secondary ion current divided by the total image intensity (the sum of all the grey values in the image) This total ion current is measured immediately after acquisition of the image with the Faraday cup or ion multiplier;

(ii) conversion of the local secondary ion intensities to local concentrations according to procedures as the local thermal equilibrium model (LTE), the matrix ion species ratio method (MISR) or the sensitivity factor method (SF)

Several ways of visualising the information are then possible including depth profiles of the entire analyzed surface or local areas of down to $10 \mu\text{m}^2$, line scan data, cross sectional information or 3 dimensional representations

presented either as a solid object or as a transparent view emphasising details within the stack of images.

Other image processing steps consist in removing shadow effects due to bright spots, uneven illuminations of the field of view or variation in detection efficiency of the secondary ions.

Ion microprobe operation. In normal microprobe analysis with the CAMECA 4f system the focused Cs^+ beam is scanned with a frequency of 20 (as an alternative 2) kHz in an intricate interlaced (digital meander) scanning pattern, which is incompatible with the (from left to right pixel-after-pixel and line-after-line) image acquisition of the KONTRON system unless cumbersome image reconstruction is applied. An illustration of the image of a copper electron microscope grid as recorded with the Cameca scan generator and the reconstructed image is given in Figure 2.

Figure 2 : Illustration of image restoration algorithm. (a) image of Cu electron microscopy grid taken with CAMECA scan generation system; (b) reconstructed image

the dwell time of the beam on each pixel. It appeared that the necessary condition, namely that the dwell time well exceeds the time-of-flight could be met provided scanning was proceeding slow enough at a maximum speed of few times 0.10 ms per pixel.

The best achievable lateral resolution with the system as modified appeared to be $0.45\ \mu\text{m}$ as obtained for submicron structures (Al thickness $1\ \mu\text{m}$ on Si-substrate) for the following experimental conditions : primary ions Cs^+ at 10 kV, primary aperture 3, field aperture 1800, contrast 150, images field $25\ \mu\text{m}^2$, dwell time 0.1 or 1 ms, raster image $10\ \mu\text{m}^2$, 256×256 pixels. As far as we could judge this result is compatible with the primary ion beam dimension and its stability

APPLICATIONS

The instrumentation described is used in a number of areas in microelectronic research and materials research. The camera systems considerably extends the detection sensitivity range of three dimensional analysis from individual secondary ions to matrix elements and hence meets the specific SIMS requirements of high dynamic range. With the KONTRON IBAS image processor ion microprobe analysis is possible at submicron lateral resolution. The following areas are exemplary for image analysis and local area depth profiling. They could not be performed with the instrument in its standard configuration.

The scanning interface of the KONTRON system was used for slow scanning ion microprobe analysis. A sawtooth signal of the scanning interface was transferred to an analog signal and amplified (with a PA 89 opamp) to 500 V to control the deflector plates of the primary ion beam taking care to synchronise primary beam rastering with image collection. Since the dynamic transfer system is not active when using the modified system, rastering is limited to $20\ \mu\text{m}$ areas. Time-of-flight aberrations of the recorded images depending on the mass dependent synchronization between scanning and image formation is function of

Determination of impurities in high purity quartz grains with dimensions of approximately 200 μm . Trace impurities are localised and range around the ppm level. To account for the small size and the dielectric nature the samples were mounted in a soft metal (indium) foil and bombarded with a 100 nA $^{16}\text{O}^-$ beam. In order to block out any signal from the impurities in the indium foil, an area measuring 100 μm in diameter well inside the particles was selected for imaging by use of an aperture at the first image plane in the microscope. The ephemeric nature of the signals and the large variation in secondary ion currents made the application of the image processing system in the ion microscope mode mandatory. Problems arose with specific impurities e.g. iron containing inclusions could be brought out from $^{28}\text{Si}_2$ dimers by representing the ratio of mass 56 to mass 28 (Si). The detection of the iron and other impurities was only possible at high detector gain settings, relying on the EDRIM method. To aid in the image analysis all image data were multiplied by a binary image of the matrix element (Si at mass 28) that is representative of the particle shape. The binary image was composed of a "zero" grey value for pixels outside of the grain and "one" for the pixels inside of the grain. The result of this operation is that any signal from outside the grain, e.g. from the indium foil was multiplied by zero and hence became zero, while the value of pixels inside the grains remained unaffected.

Figure 3a : Overall depth profile of the Al-Cu layer on a SiO_2 substrate. $^{12}\text{C}^+$, $^{14}\text{N}^+$, $^{30}\text{Si}^+$, $^{27}\text{Al}^+$, $^{63}\text{Cu}^+$ and $^{184}\text{W}^+$

Figure 3b : Local area depth profile of a 16x16 region with inadequate surface covering due to contamination with carbon during fabrication process.

Local area depth profiling in surface coatings.

The following example is exemplary of possibilities in this area. A copper containing aluminium layer is separated from a SiO_2 substrate by a shallow tungsten-titanium layer. The purpose of the measurements was to study the overall homogeneity of the substrate. Primary bombardment with argon ions (12.5 kV, 500 nA) was applied over a $250 \times 250 \mu\text{m}^2$ area and a 150 μm diameter was analyzed. Images were taken for 9 different secondary ions resulting each in 30 different measurements on 256×256 pixels. Figure 3a shows the average depth profile taken for 6 different species. Figure 3b shows the local depth profile for a 16×16 pixel square with abnormal sputtering behaviour. These local depth profiles aid considerably in understanding the multilayered structure composition and its homogeneity.

Figure 5 : Iodine distribution in AgBrI crystal

μm . Successive images were stored in the image analyzer for post-measurement image analysis. Figure 4 shows the iodine distribution in AgBrI crystal taken in these typical conditions.

Silver halogenide microcrystallites.

High sensitivity photographic film depends on tabular halogenide crystals with typically a thickness 0.1 to 0.3 μm and a triangular AgBr nucleus surrounded by a peripheral AgBrI growth. The iodine and bromine distribution is important for the photographic sensitivity. Imaging SIMS is of considerable help for the microscopical characterization of this material. Sample cooling during analysis with liquid nitrogen and the use of low primary ion currents is necessary to preserve crystallographical and compositional identity of the material. Ion microprobe analysis was necessary for successful SIMS analysis of the material. Typically, a primary Cs^+ ion current of 1 pA and a dwell time per pixel of 1 ms was used to obtain 256x256 images on an image field of 25

Acknowledgment

This work was performed with the financial aid of NFWO, Brussels, Belgium (project IIKW-4.0002.90) and the Belgian program on interuniversity attraction poles (IUAP-11 and 12). PVE is research associate of NFWO.

REFERENCES

1. B.K. Furman and G.H. Morrison, *Anal. Chem.*, **52**, 2305 (1980)
2. S.R. Bryan, W.S. Woodward, R.W. Linton and D.P. Griffis, *J. Vac. Sci. Techn.*, **A3**, 2102 (1985)
3. N.A. Thorne, A. Dubus and F. Degreève, *Scanning electron Microscopy*, **4**, 1255 (1985)
4. F. Michiels, W. Van Hoolst, P. Van Espen and F. Adams, *J. Am. Soc. Mass Spectrom.*, **1**, 37 (1990)
5. D.S. Mantus and G.H. Morrison, *Anal. Chem.*, **62**, 1148 (1990)
6. R.W. Odom, B. K. Furman, C.A. Evans Jr, C.E. Bryson, W.A. Petersen, M.A. Kelly and D.H. Wayne, *Anal. Chem.*, **55**, 574 (1983)
7. W. Van Hoolst and P. Van Espen, *Mikrochimica Acta*, in press