RESEARCH IN QUANTITATIVE X-RAY FLUORESCENCE MICROANALYSIS OF PATTERNED THIN FILMS

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ABSTRACT

The applicability of micro X-ray fluorescence (MXRF) for analysis of thin films was investigated. For the restoration of a microbeam profile of primary X-rays from a wire scan, a mathematical procedure was developed. In order to verify obtained results, a CCD camera was used for direct measurements of beam profiles. Reasonably good agreement was obtained between results of measurements and calculations. The spatial resolution of the spectrometer was determined from scans of patterned thin films. MXRF was applied in practice for measurements of thicknesses of Ti/Cu/Ti films in microtensile coupons. The results indicate non-uniformity in the thickness of Ti and Cu films with location. The uniformity and homogeneity of TiN films deposited on Si wafers was tested. Measurements confirmed that TiN films could be prepared with the required purity, stoichiometry, and thickness to produce a TiN Standard Reference Material®.

INTRODUCTION

Careful control of the elemental composition of metal alloy thin films on semiconductor wafers during the fabrication process is very important both in research laboratories and in process manufacturing in the semiconductor industry. Accurate measurements of the uniformity and composition of such films are also critical to future needs in order to advance this technology. Micro X-ray fluorescence spectrometry (MXRF) is a modern tool for examining both the uniformity and elemental composition of thin films during such operations due to its rapid data acquisition, its non-destructive nature, and its in-situ application. An important advantage of MXRF is that the primary beam can be collimated down to a very small size, on the order of tens of micrometers in diameter, allowing small structural features to be analyzed. Since less energy is deposited in the sample as a result of X-ray excitation compared to an electron excitation source, thermal damage to the sample and associated problems such as loss of volatile elements and chemical change are avoided. Sample preparation is simpler because there is no need to coat the sample with a conductive material. These characteristics of MXRF offer a capability for applications in the semiconductor industry such as simultaneous multi-elemental analysis of integrated circuits, circuit boards, ceramic chip carriers, and semiconductor wafers. MXRF analysis of patterned wafers has been investigated by Zaitz [1]. Growing interest in this method has also been marked by an increase in publications related to this subject [2,3]. During the past four years, we conducted joint research focused on measurements of microbeam profiles and on testing the uniformity of thin films on silicon and in electronic devices.
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INSTRUMENTATION

Measurements were performed with the NIST micro X-ray fluorescence spectrometer described previously [4]. Some of its important features are a small-spot X-ray source, pinhole collimators having apertures from 70 μm to 2 mm, an automatic positioning sample stage, color video imaging, a Si(Li) solid state detector with an ultrathin beryllium window, computer software for data acquisition and positioning of the sample, and a vacuum chamber.

MEASUREMENT OF MICROBEAM PROFILE

Knowledge of the beam profile and its size is necessary for obtaining optimum spatial resolution in scanning microbeam measurements. For determination of the microbeam profile from different collimators (70 μm, 100 μm, and 374 μm), we applied a simple procedure based on scanning of the X-ray beam from a collimator using a Ni wire with a diameter of 12 μm. For this purpose we scanned the wire across the beam in the Y direction (perpendicular to the plane of the detector and collimator) in 2 μm increments and measured Ni K-L2,3 X-rays. However, X-ray intensity from the wire is a result of a convolution of the beam profile and the length of wire illuminated by X-rays. Therefore, measured intensity vs. wire position are not adequate to describe the real shape of the beam profile. A non-linear, least squares procedure was developed to restore the beam profile. In this procedure, theoretically calculated intensities of characteristic X-rays excited in the wire are compared with measured intensities. It was assumed that the beam has axial symmetry and that a function describing the distribution of photon flux can be given in the form of a parametric equation. A computer program [5] was created to calculate the photon flux density from a wire scan. A variety of parametric functions were investigated and the best chi-square value was obtained using the Fermi function. In order to verify the results, a CCD camera was used for direct measurements of beam profiles from different collimators. In Figure 1, a microbeam profile obtained from the CCD camera is compared to the calculated profile in the plane across the center of the X-ray beam from a 70 μm collimator. Reasonably good agreement was obtained between both profiles. However, the overall microbeam profile measured with the CCD camera has a complex shape with a number of peaks near the center. The calculated profile is smooth, due to the algorithm employed.

In order to test the spatial resolution of the NIST spectrometer, a linear scan was performed with the 70 μm collimator across a flat Cr strip 250 μm wide and 0.1 μm thick. The measured data are presented in Figure 2 where the x-axis values indicate the center of the X-ray beam. As the beam begins to cross the Cr strip, the Cr K-L2,3 count rate increases until the entire beam illuminates the strip. The region of maximum count rate covers a width of only 150 μm. Therefore, it is clear that only 60% of the strip width can be used to evaluate its uniformity. Efforts are underway to use the real beam profile in combination with mathematical procedures, e.g. Fourier transform or serial multiplication inversion, to improve the spatial resolution of linear scans of patterned samples.
Figure 1. Calculated (continuous curve) and measured (dots), by CCD camera, profiles of the X-ray beam from a 70 μm collimator.

Figure 2. Results of linear scan of Cr strip of 250 μm width. The bars represent uncertainty due to counting statistics (1 standard deviation).
TESTING THE UNIFORMITY OF THIN FILMS IN AN ELECTRONIC DEVICE

In the case of analysis of multilayer thin films, a major source of error could be caused by spectral interference between a characteristic X-ray line and a diffraction peak. Just such a situation occurred during the analysis of Ti/Cu films where a diffraction peak overlaps the Ti K-L$_{2,3}$ lines. The diffraction peak can be shifted from the region of interest by changing the incidence or take off angles. However, that is impossible to do in our spectrometer. We found that the diffraction peak can be removed from the spectrum by filtering the primary X-rays using 80 μm thick Al foil with a corresponding reduction in Ti count rate by a factor of about 3.

MXRF was applied to investigate the uniformity of thin films in microtensile coupons. The measured specimens consist of a Si frame with a window through the center about 1 mm long and 1.5 mm wide. A single tensile strip 200 μm wide by 600 μm long is suspended across the window. The strip is a multilayer film consisting of an adhesion layer of 0.05 μm of Ti covered by 1.1 μm of Cu and a second, cap layer of 0.05 μm of Ti. Scans of the strip were performed along its entire length, including the suspended center section and both end sections supported on silicon, using an X-ray microbeam from a 70 μm collimator. The time of measurement of each pixel was 3000 seconds. The thickness of the Ti and Cu layers were calculated using a fundamental parameters procedure incorporated into Toolbox Software [6]. Single element, thin film standards of Ti and Cu were used for calibration of the procedure. For Ti, the total thickness of the two Ti layers was computed. Figure 3 shows the variations of Cu thickness in different areas of the strip. The same information obtained for Ti is presented in Figure 4. The results are in reasonably good agreement with the thickness determined using a quartz-crystal thickness monitor during preparation of the strip [7]. It is worth mentioning that the thickness of Cu film in the central part of the strip is lower than close to the ends. The total thickness obtained for two Ti layers does not show such a relation. The results in Figure 4 appear to indicate non-uniformity in the Ti thickness with location in a random fashion. The precision of thickness results for Ti is much poorer but not due to counting statistics. Since, this approach did not allow us to determine the thickness of each individual Ti layer, we are investigating ways to do so.

DETERMINATION OF UNIFORMITY OF PROTOTYPE TiN THIN FILMS

As was mentioned previously, X-ray fluorescence spectrometry is often used in the semiconductor industry. For calibration of the measurement process, thin films of the same type having known composition and thickness are required. For this purpose, prototype films of TiN with nominal thickness of 100 nm on silicon wafer substrates of 7.6 cm diameter were prepared by argon ion-beam sputtering from a commercial TiN target. Fabrication and characterization of such a film was described by Pella et al. [8]. X-ray fluorescence indicated that the purity of the films was acceptable. Aside from argon, the only contaminants detected were Cr, Fe, and Ni introduced from the stainless steel sputtering chamber. The TiN coated wafer was to be divided into platelets to provide the actual samples for the user community. Therefore, it was important to maximize the film uniformity over most of the wafer. The uniformity and homogeneity of the film deposit were measured by MXRF by step scanning an X-ray beam from a 1 mm diameter
Figure 3. Results of measurements of Cu thickness in tensile coupons. The bars represent uncertainty due to counting statistics (1 standard deviation).

Figure 4. Results of measurements of Ti thickness in tensile coupons. The bars represent uncertainty due to counting statistics (1 standard deviation).
Figure 5. X-Ray fluorescence scan showing variation of TiN film thickness across the diameter of a 7.6 cm silicon wafer. The bars represent uncertainty due to counting statistics (1 standard deviation).
collimator across the diameter of the wafer. The results of measurements, shown in Figure 5, indicated that the film thickness near the edges of the wafer was about 5% lower than near the center. It was found that such TiN films could be prepared with the required purity, homogeneity, stoichiometry and thickness to create a TiN Standard Reference Material®.

CONCLUSIONS

The results of this research confirmed that X-ray fluorescence microanalysis with a collimated microbeam can be successfully applied for testing uniformity of thin films prepared by ion sputtering techniques. For imaging of patterned samples, this technique can be satisfactorily used for analysis of small features with dimensions larger than the size of the X-ray beam spot on the surface of the sample. With a 45°/45° spectrometer geometry and a 70 μm collimator, features have to be larger than about 105 μm. Mathematical procedures that can be used for improving spatial resolution require further investigation.

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REFERENCES