XPS AND EDS INVESTIGATIONS OF QUARTZ RESONATOR ELECTRODES FOR USE IN QUARTZ CRYSTAL MICROBALANCE

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ABSTRACT

XPS, EDS and microstructural measurements for the analysis of the electrode material of a quartz resonator of a QCM model PC-2 have been carried out. The results show that Ni has been used for the electrode deposition on a precision quartz resonator for use in a commercial QCM procured by the NPL for aerosol measurements.

INTRODUCTION

Quartz crystal microbalance (QCM) is an effective solid state sensor that is currently used for environmental monitoring such as aerosol concentration and other pollutants in the atmosphere. It is based on the change on acoustic properties due to the piezoelectric effect of quartz crystals. The most common transducer for such purposes is a shear mode AT-cut quartz resonator. The QCM comprises of an AT-cut quartz crystal sandwiched between two metal excitation electrodes that generate transverse shear wave across the thickness of the quartz crystal. Figure 1 depicts some typical resonators where on the quartz disks, electrodes are deposited by vacuum evaporation techniques. The crystal resonator upon excitation oscillates in the thickness-shear mode where the top and the bottom surfaces of the oscillating crystal execute vibrations in opposite phases.

Figure 1: A typical arrangement of a thickness-shear AT-cut quartz resonator assembly.

It may be mentioned here that the frequency of a thickness-shear resonator is given by the expression

$$f = n/2\pi (c'/\rho)^{1/2}$$

where ***n*** is the overtone number, ***t*** is the thickness of the crystal, Δ is the density, and ***c!*** is the rotated elastic modulus. The elastic modulus and the density are the *primary materials factors* that determine the crystal frequency. The elastic modulus represents a type of average of the interatomic force constants. Thus, it should be sensitive to the substitution and /or modification of impurities and defects in the crystal lattice. Other factors such as piezoelectric coupling, resonator contour, and mounting structure also play a role in the actual frequency of the quartz device. It is in this perspective that a non-destructive study of the electrode material becomes important.

Sensors are designed such that the propagation characteristics of these waves like their phase velocity and/or their attenuation coefficient are affected by the measurands of interest. The shear waves experience an antinode at the surface of the quartz crystal. Thus, if an adhesive film onto the electrode material is attached, the shear wave generated by the quartz transducer can propagate into the film on the surface of the crystal. The thickness or the mass per unit area of the film and the nature of the shear wave propagation in the film determine the frequency response. The mass change is generally determined from the frequency response according to the relation given by

$$\Delta f = -2f_0\Delta m/A(\rho_q\mu_q)^{1/2}$$

where Δf is the measured frequency shift, $f0$ is the initial resonant frequency, Δm is the mass change, A is the piezoelectrically active area defined by the two active electrodes, ρq is the density of quartz = 2.648 gm/cm3 , μq is the shear modulus = 2.947 x 10 11 dynes /cm2 for AT-cut quartz.

The ability of quartz crystal to respond to small changes in mass at its surface has led to many fundamental investigations of interfacial phenomena of technological significance. These devices are becoming increasingly appreciated in that sensors can be readily designed by appropriate modification of the transducer. Different acoustic wave sensors such as shear, surface acoustic, flexure and shear horizontal acoustic plate mode devices are in use to date for the detection of biologically significant analytes, metal ions and nerve toxin analogs etc. These devices generally rely on interfacial chemical events that result in mass changes, which alter the frequency of the acoustic waves that propagates through the transducer and the chemically active film. Current research interests include the investigation of novel biocompatible materials for the sensor/sample interface and the advancement of membrane-based electrochemical and quartz crystal based sensors for medicine, food and the environment.

We present in this paper the results of our investigation on XPS, EDS and microstructural measurements for the analysis of the electrode material of a quartz resonator of a QCM model PC-2. The results show that Ni has been used for the electrode deposition on a precision quartz resonator for use in a commercial QCM procured by the NPL for aerosol measurements.

EXPERIMENTAL

We have done XPS (X-ray induced photon spectroscopy) and EDS (Energy Dispersive Spectroscopy) measurements for the analysis of the electrode material of a quartz resonator of a QCM model PC-2 from California Instruments. The crystal resonators oscillate at 10 MHz fundamental mode frequency. Investigations were performed on the as-received sample and after sputtering to remove any surface contamination. The analysis was done by the XPS system of Perkin-Elmer Model 1257, which consists of a dual anode (Mg Kα/Al Kα) X-ray source and a 285 mm radius, high resolution Hemispherical Electron Energy Analyzer. The sample under analysis was mounted on a high precision x, y, z, θ manipulator inside a UHV chamber of base pressure 5 x 10^{-10} Torr. Figure 2 depicts a pictorial view of the experimental set up. The XPS analysis was done by a 15 kV, 100W, MgKα source, and the secondary electrons emitted were analyzed with the analyzer normal to the sample surface. The low resolution survey scans and high resolution core level spectra were taken with pass energy of 100 eV and 40 eV respectively. The surface was sputtered by using differentially pumped Ar^+ ion source of 4 KV at an etch rate of approx. 10µ per minute.

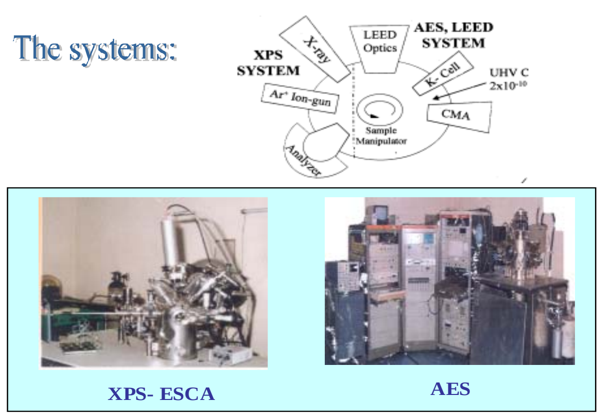


Figure 2: A pictorial view of experimental set up

RESULTS AND DISCUSSION

The XPS results on as-received sample showed peaks of Ni, Co, Fe, Ag, and C. The peaks of Fe and Co were that of the sample holder. The peak for Ag is supposed to be due to the silver paste used in mounting the resonator for contacts. The sample was then sputtered by Ar^+ ion source of 4 KV at an etching rate of 10μ/minute/μA, for 5 min at 2 μA. This sputtering was approximately 100μ. The position of the sample was shifted to new position for XPS, so that all the X-rays were falling on the contacts of the sample. It was found that all the contamination (Carbon and Oxygen) on the surface was removed after the sputtering. Figure 3 shows the results. Figure 4 shows the EDS spectrum from the surface of the quartz sample. Figure 5 and 6 show the surface topography of the quartz –electrode interface and the bare quartz area.

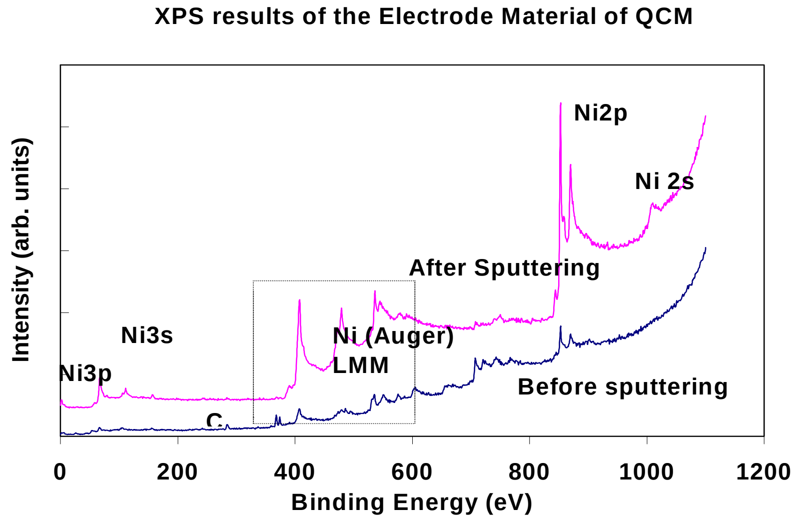
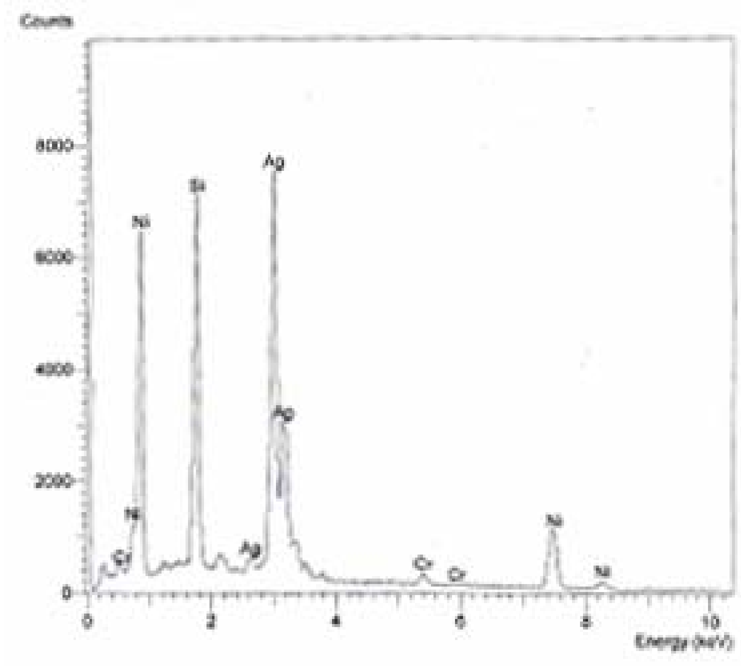
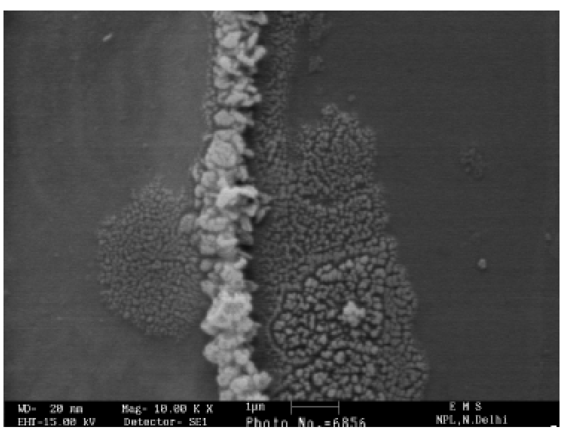


Figure 3: XPS spectra of the electroded region of the QCM quartz resonator in its as-received state (before sputtering) and after sputtering



substrate signals
DEPTH RESOLUTION ~3 MICRONS-

.Figure 4: EDS spectrum depicting different substrate signals from the surface of the quartz resonator



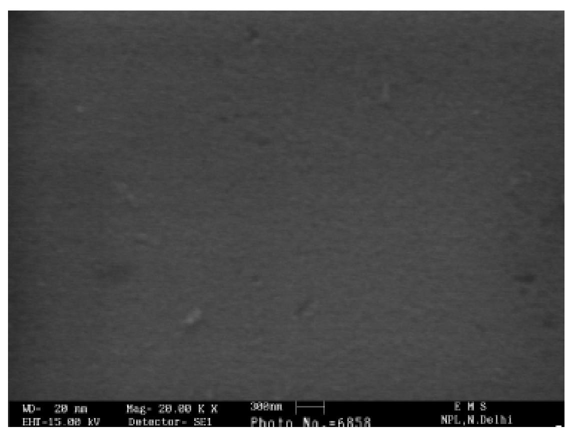


Figure 5. SEM micrograph depicting surface
topography of quartz-electrode interface

Figure 6. SEM micrograph depicting surface
topography of quartz

CONCLUSION

The present investigations have shown that the electrode surface after sputtering was entirely made of Ni and no other trace of elements was found on the surface. Microstructural and EDS analysis have also been conducted. It appears that that the use of Ni has been made for the electrode deposition on a precision quartz resonator for use in a commercial QCM procured by the NPL for aerosol measurements.

An added use of Ni can be envisaged in using QCM as a magnetic sensor in which quartz frequency would be affected by the electrode stress onto the quartz disk due to magnetostriction.