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Tantalum pentoxide – based quartz crystal microbalance for NH_3 detection

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This work presents the abilities of a thin Ta_2O_5 film coated QCM's (Quartz Crystal Microbalance) to detect NH_3 concentrations in a range 10 to 10000 ppm. The active layers of Ta_2O_5 (86 and 286 nm) are deposited by e-beam evaporation. The morphology of the Ta_2O_5 films is studied by Transmission Electron Microscopy. The chemical compositions of the evaporated source material and obtained films are investigated in details by X-ray Photoelectron Spectroscopy. The Ta:O ratio is approximately 1:3 in the source material as well as in the films. This ratio shows a negligible change for different film thicknesses. The dielectric properties of Ta_2O_5 are obtained from volt-capacity and ellipsometric measurements. The sorption abilities of QCMs with thin Ta_2O_5 are determined by measuring the resonance frequency shifts of the QCM over aqueous solutions of NH_3 with different concentrations. The maximum response of the QCM increases when the film thickness and NH_3 concentration rise. The minimal detectible concentration is found to be 10ppm NH_3. The character of the sorption process is defined as physical. Based on experimental results, the sorbed mass of NH_3 is calculated for the whole investigated interval. The investigations present the possibility to monitor NH_3 by a QCM with Ta_2O_5.

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Keywords: QCM, Ta_2O_5, Gas sensors

1. Introduction

Environment pollution encourages the development of a sensor system for gas detection. For this purpose, the use of Quartz Crystal Microbalances (QCMs) is suitable, due to their response to surface mass loading. The sensitive layer deposited on the QCM acts as a pure mass detector, sorbing the gases from the surrounding environment, resulting in a change of the QCM's frequency. Suitable coatings for the QCM can be polymer layers, sol-gel films [1-2] or inorganic oxides [3-4]. The sensitivity of the QCM depends on the coating properties such as: structure, adhesion, chemical composition, and on the compatibility of the deposition processes with QCM technology. The aim of this paper is to study the chemical composition and dielectric properties of e–beam evaporated Ta_2O_5, as well as the sorption abilities for ammonia.

2. Experimental

The investigated structures were created on 8 nm diameter AT-cut polished quartz wafers. Silver electrodes were formed on each side of the plates, with 4 mm diameter and 1200 Å thickness. A quartz crystal monitor measured the electrode thickness during the deposition. The resulting resonant frequency was 14 MHz. The equivalent dynamic parameters of the structures were measured by a Selective Level Meter.Both sides of the prepared piezoelements were covered with a thin Ta_2O_5 dielectric layer, by electron beam evaporation of a Ta_2O_5 powder source. The process was carried out at an initial vacuum of 7×10^{-6} torr, an operational-mode vacuum of 3×10^{-5} torr, an anode current of 50 mA and a calculated power of 350W, with a deposition rate of 28 nm/min. The thickness of the Ta_2O_5 layers and the deposition rate were controlled with a Digital Thin Film Deposition Monitor MSV-1843/H MIKI-EEV. The refractive index and thickness of the dielectric layers were determined ellipsometrically (λ = 632.8 nm) by measuring control silicon wafers placed next to the piezoelement during the deposition. In order to determine the dielectric constant, Ta_2O_5 films were deposited on n-type silicon. Capacitors were formed using a mercury probe for the upper contact (area 4.5×10^{-3} cm^2) on the films. The accumulation capacitances were measured at 1MHz using a Boonton 76A Capacitance Bridge. The morphology of the thin layers was analysed by TEM (Philips–400). The samples were prepared for observation using a two-step replica gelatin-carbon-platinum process. XPS analyses were performed on a Kratos AXIS ULTRA with an Al K_α X-ray source (1486.6 eV) and a resolution of 0.4 eV, as determined from the analysis of the Co Fermi edge. The base pressure was ~ 10^{-8} Pa. The photoelectron take-off angle was 0º (normal to the surface); the analysis spot size was 700×400 μm. The sorption ability of Ta_2O_5 was determined from the measured time-frequency characteristics of QCMs covered with thin Ta_2O_5 layers. The measurements were based on the correlation between the frequency shift and additional mass loading of the resonator. Sauerbrey [5] developed an empirical equation for AT–cut quartz, describing the relation between the mass of the thin film deposited on the quartz crystal and

the corresponding change in the resonant frequency. This allows the absorbed mass to be calculated. The QCMs were consequently kept over NH_3 solutions with different concentrations in a special thermostable chamber, and the frequencies were measured by a frequency counter. The QCMs were initially saturated over water vapour, to avoid its influence on the NH_3 sorption. The frequency of saturation obtained over water was used as initial level for subsequent measurements over NH_3 solution. The experimental set-up and the methodology of the measurement are described in detail in [6].

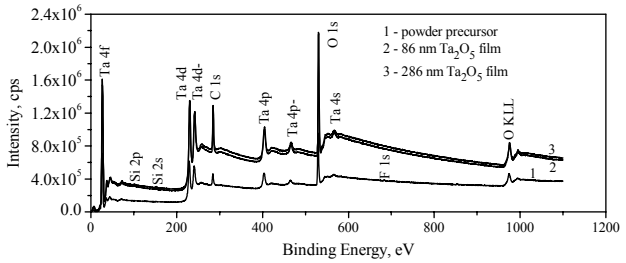

Fig. 1. XPS survey spectra of the precursor, 286 nm and 86 nm Ta_2O_5 films on Si substrates.

3. Results and discussion

The dielectric properties of the Ta_2O_5 films were measured on control Si wafers, covered with Ta_2O_5 along with the QCM. E–beam evaporated Ta_2O_5 layers have similar characteristics to those of chemical vapor deposited films [7]: a refractive index of 2.07 and a dielectric constant of 21,4. The TEM image of Ta_2O_5 films (86 and 246 nm thick) showed an amorphous structure. Crystal fractions with sizes ranging from 0.1 to 1 μm in the films' amorphous matrix were also observed. A more homogeneous surface was detected with increasing layer thickness. The investigations confirmed the possibility to obtain by evaporation amorphous Ta_2O_5 at room temperature.

Fig. 1 illustrates the XPS survey spectra of the powder precursor and two Ta_2O_5 films of different thickness. All three spectra consist of well defined XPS lines of Ta 4f, 4d, 4p and 4s; O 1s; C 1s; and an Auger O_{KLL} line, demonstrating that the composition of the films is practically the same as the precursor one. A relatively strong C1s feature is observed at ~ 284.3-284.9 eV for the precursor and deposited films, most likely as a result of hydrocarbon adsorption on the samples' surfaces due to the exposure after the deposition to atmospheric air. (In-situ surface cleaning using an ion-gun was not applied, in order to avoid the negative effects of the sputtering on the film composition.). The carbon signal was used to take into account the effect of the samples' charging during the measurement. All binding energies of the high-resolution spectra were calibrated with a C 1s binding energy of 285.0 eV. Apart from Ta, O and C lines, the precursor's spectrum also contains a low intensity feature corresponding to F 1s, indicating the presence of a small (0.98 at%) amount of F in the precursor substance. This contamination might be due to the glass container used to store the precursor. The F 1s line is not found in the spectra of the deposited films, i.e. the obtained layers are fluorine free. The spectra of the evaporated Ta_2O_5 films show additionally two low-intensity XPS lines characteristic of Si (Si 2p and Si 2s). The Si 2p feature is placed at 101.9 and 101.3 eV, with an intensity corresponding to 1.16 and 1.07 at % for the 246 nm and 86 nm films respectively. The location of the Si 2p peaks suggests that the Si atoms are bound to O, forming the intermediate silicon oxidation state Si^{2+} (SiO) [8]. Most probably, the Si features originate from Si substrate. Fig. 2 shows high-resolution Ta 4f and O 1s XPS spectra of the investigated structures and the powder precursor. The Ta 4f spectrum of the precursor consists of two pronounced peaks (first at 25.2 eV and a second one at 27.7 eV with a slightly higher intensity) followed by a shoulder in the range 28-30 eV. The overall shape of the line, peak positions and their energy separation (~ 2.5 eV) are not consistent with the Ta 4f doublet of shoichiometric Ta_2O_5. Ta 4f doublets typical of Ta_2O_5 have two peaks: Ta $4f_{7/2}$ at ~ 26.0-26.6 eV and Ta $4f_{5/2}$ at the binding energy 1.9 eV higher [9,10]. The intensity of the Ta $4f_{7/2}$ peak is higher than that of the Ta $4f_{5/2}$ one. So, the Ta 4f spectra of the powder can be considered as a sum of doublets attributed to some Ta suboxide states (Ta^{4+} and Ta^{3+} as indicated from the positions of the peaks) and of Ta_2O_5. The intensity of the suboxide doublets is higher and they dominate the spectra, whereas the doublet from stoichiometric Ta_2O_5 is mainly responsible for the shoulder observed at 28-30 eV. It can be concluded that the precursor's chemical composition is TaO_x rather than stoichiometric Ta_2O_5. The Ta 4f lines of the deposited films, however, agree well with the Ta 4f doublet representative of the Ta-O bond in Ta_2O_5. The Ta$4f_{7/2}$ peak is placed at 26.0 and 26.2 eV, and the Ta $4f_{5/2}$ one is at 28.2 and 28.3 eV for the 246 nm and 86 nm films respectively. These results clearly demonstrate that the deposited films are stoichiometric Ta_2O_5, i.e. the deposition conditions ensure that the obtained layers have the desired composition. The O 1s spectra (Fig. 2b) further support this assumption. The O 1s peaks of the deposited layers are centered at binding energies of 530.6 and 530.7 eV for the 246 nm and 86 nm layers respectively, which is consistent with reported data for Ta_2O_5 [11]. The FWHM of both peaks is 1.92 eV. The oxygen spectrum of the precursor is located at lower binding energies (530.3 eV). It is broader than the spectra of the evaporated films and is distorted towards higher energies, confirming the conclusions on precursor's substoichiometry made from the Ta 4f spectral line. The O/Ta ratio estimated from the spectra is ~ 3 for all samples, including the precursor,

which is somewhat higher than the maximum theoretical value of 2.5. This is thought to result from the absorption or trapping of oxygen from the air to the sample surfaces.

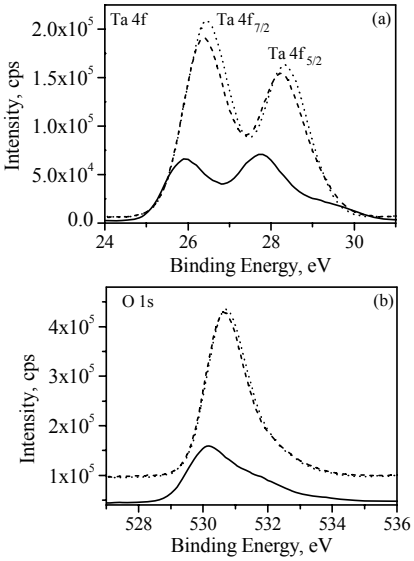

Fig. 2. Ta 4f (a) and O 1s (b) XPS spectra of the precursor (——), 246 nm (-----), and 86 nm (·····) Ta_2O_5 films.

Fig. 3 shows typical time frequency characteristics of a QCM with an 86 nm Ta_2O_5 film. Curve 1 shows the saturation over water. The measured difference between the QCM saturation frequencies in air and those over water was 100Hz. Curve 2 presents the QCM frequency change over a 500 ppm NH_3 aqueous solution.

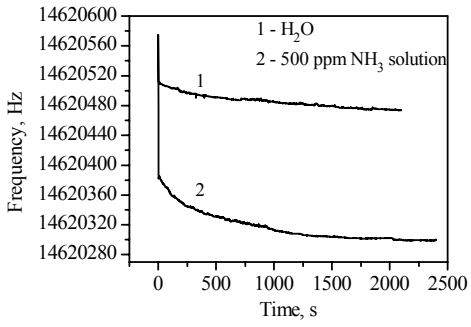

Fig. 3. Time-frequency characteristics of a QCM with an 86 nm Ta_2O_5 film, during saturation.

The NH_3 sorption by the Ta_2O_5 layers was estimated as the difference (Δf) between the frequency saturation over water and that over the investigated ammonia solution. The Δf value in the case of saturation over 500 ppm NH_3 was calculated to be 173 Hz, which corresponds to a 44.98 ng sorbed mass. Both curves (1 and 2) show a similar behavior – rapid sorption followed by slow saturation. The dependence can be expressed as an exponential function: $f = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x_0/t_2}$, ($y_0$ is the initial frequency, x is the time and A_1, A_2 ,t_1,and t_2 are coefficients). The relation is valid for all measured time frequency characteristics with the coefficients being adjusted for each case. The QCM's sorption ability to NH_3 vapors was studied in the concentration range 10 to 10000 ppm, with 86 and 246 nm Ta_2O_5 layers. For each NH_3 concentration and Ta_2O_5 thickness, the time frequency characteristics were measured and the sorbed mass was calculated. Fig. 4 presents the NH_3 sorbed mass (Δm) as a function of the NH_3 concentration. Curves 1 and 2 illustrate the Δm changes of QCMs covered with 86 nm and 246 nm Ta_2O_5 layers respectively. An increase in the NH_3 concentration results in a Δm rise, which shows that, the sorbed ammonia quantity increases. The Δm value for a constant concentration of 100 ppm NH_3 was 26.52 ng for QCMs with 86 nm Ta_2O_5, while for those with 246 nm it was almost two times higher (49.61 ng). For a 5000 ppm NH_3 concentration, the calculated values were 68.64 and 120 ng respectively. The sorption dependence on the thickness of the layer confirms that the sorption mechanism is based on diffusion. Both curves of fig.4 plotted on a semi-logarithmic scale show linear behavior, with a difference only in their slope. After completion of the measurement, the QCMs recovered their initial frequencies as result of desorption. The process occured without applying any additional energy, which supports the physical character of the sorption. Similar results were obtained in QCM experiments with SnO_2 and TiO_2 films [6,12] and polymer layers [13].

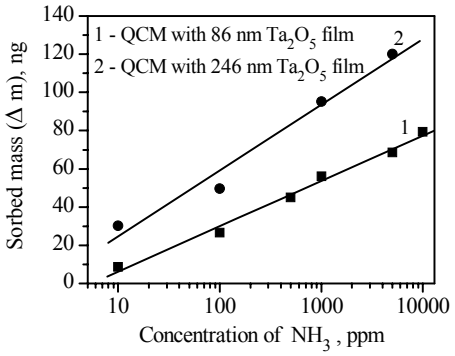

Fig. 4. Dependence of the sorbed mass vs. the NH_3 concentration.

4. Conclusion

In this work, we present the possibility to monitor NH_3 by a Ta_2O_5 based QCM. The mass sensing properties of the Ta_2O_5 were investigated over a wide range of NH_3 concentration, and the minimal detected one was found to be 10 ppm. The sorption process was defined as physical and reversible. It was found that the sorption process depends on the NH_3 concentration and the film thickness. The E- beam evaporated thin Ta_2O_5 films' properties, such as chemical composition, morphology, dielectric constant were also investigated. Based on the obtained results, the

main conclusion is that QCMs covered with Ta_2O_5 are suitable for NH_3 detection.

Acknowledgements

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