Chapter 77
Quartz Crystal Microbalances for On-line Monitoring of Nanostructures Growth

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Abstract Quartz Crystal Microbalances (QCM) are widely used for monitoring materials growth in vacuum physical deposition techniques; as a more complex application, QCMs are also used for on-line monitoring of thin films deposition in liquid thanks to electrochemical reactions onto quartz electrode (EQCM). Our goal here is to demonstrate that QCMs can also be used for on-line monitoring of hydrothermal nanostructures growth as well as for obtaining information on the synthesis reaction kinetic. In practice, first, we model the QCM in solution by means of a lumped element circuit; afterwards, rather than only the resonant frequency, we measure the entire QCM admittance spectrum around the resonant frequency, thus obtaining more information. As an example, we show that this approach allows to clearly distinguish the growth of different types of ZnO nanostructures, namely nanorods and nanoplatelets, on the QCM surface and the reaction dynamics.

Introduction

When the QCM is used as a gravimetric sensor, usually, only the resonant frequency is monitored [1] and the Sauerbrey equation is used to correlate the small mass loading (Δm) onto the QCM surface to the variation of the resonant frequency (Δf). The Sauerbrey equation is $\Delta f = -2 \cdot f_0^2 \cdot \Delta m/(\eta_q \cdot \rho_q)^{1/2}$ [2], where η_q is the density and ρ_q is the shear modulus of the quartz crystal, while f_0 is the original resonant frequency of the QCM. Kanazawa et al. [3] firstly investigated QCM behavior in liquid environments and found that the resonant frequency varies with the type of surrounding

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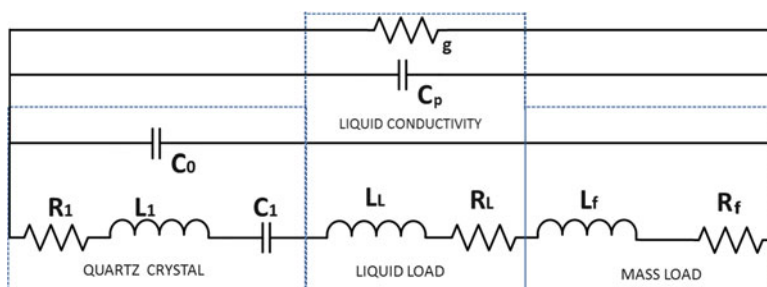
Fig. 77.1 The lumped circuit model used to represent the QCM behavior during nanostructure growth

liquid, according to the following formula: $\Delta f = -fr^{3/2}(\eta_L \cdot \rho_L/\pi \cdot \eta_q \cdot \rho_q)$, where η_L and ρ_L are the liquid viscosity and density, respectively. This pioneering work opened the door to many studies of monitoring in liquid thin films deposition by using QCM devices (e.g. see the review [4]). Martin et al. [5] demonstrated that, in liquids, if only the resonant frequency is monitored it is not possible to distinguish a mass loading contribution from a liquid property change. Therefore, in order to fully control the hydrothermal deposition process, it is necessary to analyze all the information of the recorded admittance spectra. Following [6] we developed a lumped circuit model to describe the QCM physical acoustic resonance, extending the classical Butterworth-Van Dyke model for the operation of the QCM in air. The circuit is represented in Fig. 77.1, with the original four element BVD model (R_1, L_1, C_1, C_0) and the separated contributions from the Kanazawa equation (L_L, R_L), from the mass load during nanostructure growth (L_f, R_f) and from the salty solution conductivity (C_p, g).

Experimental

We prepared the nutrient solution for the hydrothermal growth by mixing zinc nitrate and HMTA salts bought from Sigma Aldrich with a concentration of 5 mM for each reagent. We used two different AT-cut QCMs, one oscillating at 10 MHz with gold electrodes and one oscillating at 3.6864 MHz with silver electrode. On top of the silver QCM it was deposited a ZnO seed layer by dip coating in a solution of zinc acetate (0.75 M) in ethanol and ethanolamine (200:9 ratio) and successive annealing at 300 °C. Both QCMs were cleaned in acetone for 5 min prior to nanostructure growth. Each QCM was inserted inside a pyrex container with the nutrient solution and kept vertical; then, all the system was heated at 90 °C for more than 10 h. The QCM admittance spectra were continuously recorded during the hydrothermal growth by an Agilent E5070 network analyzer, acquiring separately the real and the imaginary parts.

Results and Discussion

In Fig. 77.2a, b we report the admittance spectra recorded during the growth of ZnO nanowires (NWs) on the gold QCM. Figure 77.2c shows that both the resonant frequency and the quality factor of the resonator decrease with time, due to gradual increase of the mass deposited on the microbalance. As shown in Fig. 77.2d, NWs are randomly oriented because of the unpolished QCM surface.

Interestingly, while at the beginning of the growth the resonant frequency (f_r) decrease linearly, the Q factor, which is related to the dissipation of the stored acoustic energy, decrease exponentially, thus indicating that the quality of the resonator is immediately reduced by the increase of the QCM surface roughness. Looking to the f_r behavior the mass loading seems to stop after 4 h, while the Q factor value is already stabilized after about 2 h of growth time.

Figure 77.3a shows the ZnO nanosheets (NSs) formed during the hydrothermal growth on top of the QCM with silver electrodes. The nanosheets, as measured by Energy Dispersive Spectroscopy (EDS), are composed only by Zn and O elements, even if a very small Ag contamination inside the ZnO NSs cannot be excluded (see Fig. 77.3b). The resonance frequency shift is linear with time, indicating a constant growth rate, as in the previous case of ZnO NWs; however, in contrast with the NWs experiment, the resistance (which is inversely proportional to the Q factor) increases
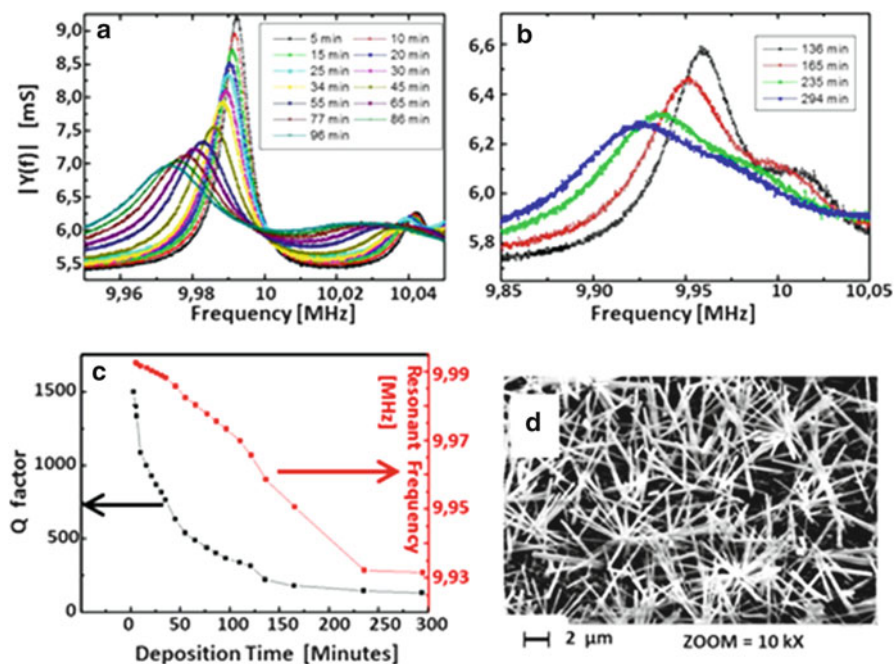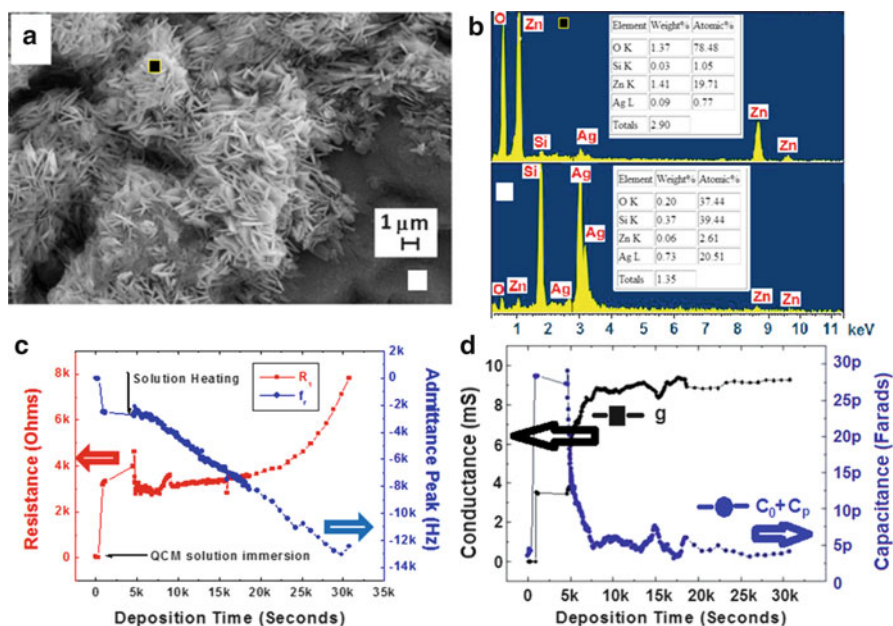

Fig. 77.2 (**a**, **b**) QCM admittance spectra recorded at different instants during NWs growth. (**c**) Resonant frequency and Q factor as a function of deposition time. (**d**) SEM image of the grown NWs

Fig. 77.3 (**a**) SEM image of the nanosheets grown on top of the quartz silver electrode. (**b**) EDS analysis of ZnO NSs (*black square*) and QCM electrode (*white square*). (**c**) R_1 and f_r and (**d**) g and ($C_0 + C_p$) as a function of deposition time

abruptly only after about 4 h of growth, see Fig. 77.3c. We attribute this different behavior to the compact microstructure of the NSs film and to a lower kinetic of the reaction that goes on for more than 10 h. Figure 77.3d shows the parameters g and C_p after QCM immersion into the nutrient solution and after the temperature variation from room temperature to 90 °C.

Conclusions

Here we demonstrated on-line monitoring of nanostructures hydrothermal growth; our approach allows to clearly distinguish different ZnO nanostructures (quasi-1D nanowire and quasi-2D nanosheets) by means of admittance spectra measurement as well as to obtain information on the synthesis reaction kinetic.

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