

ZnO NANOCRYSTALLITES OBTAINED BY OXIDATION OF ZINC ARACHIDATE – ARACHIDIC ACID LB MULTILAYERS

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Formation of ultrathin and homogenous metal oxide films has been reported by either direct oxidation¹ or oxidation subsequent to UV treatment of precursor Langmuir-Blodgett (LB) multilayers². In the present work, the direct oxidation method has been exploited to form uniformly distributed, isolated and nearly mono-disperse nanocrystallites of ZnO on quartz and freshly cleaved mica substrates using zinc arachidate - arachidic acid (ZnA - AA) composite LB multilayers as precursors.

ZnA LB multilayers transferred at different subphase pH in the range 5.0 to 6.2 have been studied by X-ray reflection (XR) and Fourier transform infrared spectroscopy (FTIR). Fig. 1 shows the FTIR spectra in the region 1300 cm^{-1} - 1800 cm^{-1} for ZnA multilayers. These results show that as the subphase pH is lowered, there is a gradual decrease in the intensity of the carboxylate asymmetric stretching band (at $\sim 1539\text{ cm}^{-1}$) and increase in the intensity of C=O band (at $\sim 1700\text{ cm}^{-1}$), indicating a decrease of ZnA content with a corresponding increase of AA content in the multilayers. The X-ray reflection (XR) studies of the multilayers transferred at different subphase pH showed the presence of single phase layered structure (with bilayer period of 47 \AA) in all the multilayers. However, the intensities of the Bragg peaks are found to diminish with decreasing subphase pH. These observations suggest mixing of ZnA and AA at molecular level and decrease of zinc content with decrease in subphase pH.

The precursor ZnA-AA multi-layers were oxidized in air at 400-700 °C. The XR patterns of ZnA-AA multilayers oxidized at 150 °C show the disappearance of Bragg peaks, which suggests the complete destruction of layered structure. FTIR studies of the oxidized multilayers showed that with increase in annealing temperature, the intensities of IR bands corresponding to various organic groups decrease and finally disappear in the case of the film oxidized at 400 °C. This indicates the complete removal of organic moieties at the oxidation temperature of 400 °C. UV-Visible studies of ZnA-AA multilayers at different oxidation temperatures corroborate the FTIR observations and show the appearance of absorption edge of zinc oxide subsequent to oxidation at or above 400 °C.

ZnA-AA mixed multilayers having different ZnA contents were oxidized at 700 °C and their optical absorption and surface morphology were studied by UV-Visible spectroscopy and atomic force microscopy. Typically, the ZnA multilayers transferred at a subphase pH of 6.2 on quartz substrates and oxidized above 400 °C show the absorption edge at $\sim 3.2\text{ eV}$, close to the bulk band gap of ZnO. The multilayers transferred at a lower subphase pH, of 5.0, with much reduced zinc content and oxidized at 700°C also show a weak absorption edge at $\sim 3.0\text{ eV}$ (Fig. 1(b)). The AFM image of a 15 monolayer ZnA film transferred at a subphase pH of 6.2 shows the presence of $\sim 2\text{ }\mu\text{m}$ clusters of nanocrystallites having size 20-40 nm (not shown here). In contrast, the AFM image of a 15 monolayer ZnA films transferred at subphase pH of 5.0 and oxidized at 700°C shows a large number of nanocrystallites of average size $\sim 10\text{ nm}$. In order to further decrease the ZnA content in the precursor ZnA-AA

multilayers and obtain isolated nanocrystallites, LB films with lesser number of monolayers were transferred at subphase pH of 5.0. AFM studies of these multilayers showed a decrease in spatial density and narrowing of size distribution of nanocrystallites with decreasing number of monolayers in the precursor multilayer. Fig. 2 shows a typical AFM image of a seven-monolayer LB film on mica substrate, oxidized at 700 °C. This image shows uniformly distributed isolated nanocrystallites of average size $\sim 11 \pm 3$ nm. Most of the nanocrystallites were in a narrow size range of 10 - 15 nm. Thus, the control of zinc content of the precursor LB multilayers achieved through proper selection of subphase pH and number of monolayers is seen to result in a reduced surface density of isolated nanocrystallites with a narrow size distribution.

References:

- [1] M. Parhizkar, N. Kumar, P.K. Nayak, S. Singh, S. S. Talwar, S. S. Major and R. S. Srinivasa. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **257–258** (2005) 445.
 [2] M. Schurr, M. Seidl, A. Brugger and H. Voit, *Thin Solid Films*, **342** (1999) 266.

Figures:

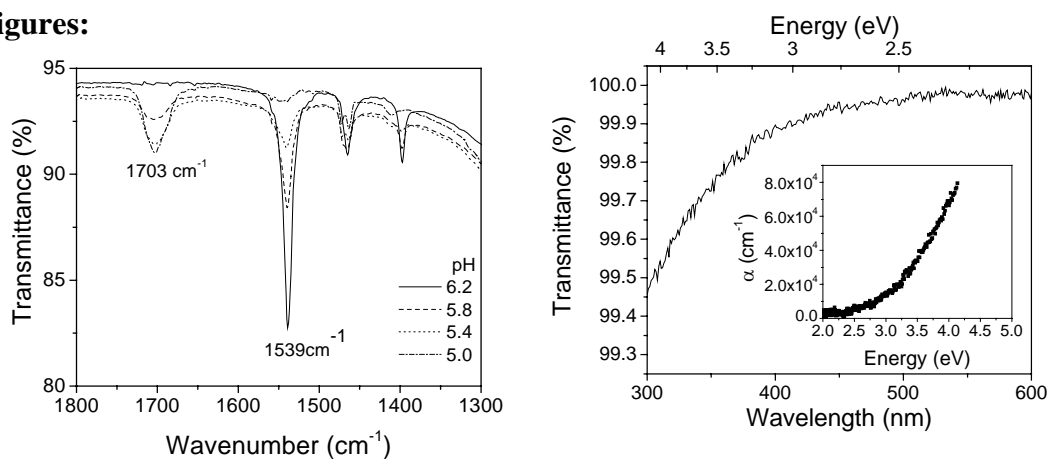


Fig. 1. (a) FTIR transmission spectra of ZnA - AA composite multilayers in the range 1300 - 1800 cm^{-1} , transferred at different subphase pH values. (b) UV-Vis. spectrum of nanocrystalline ZnO obtained by oxidation at 700°C of 15 monolayer ZnA-AA LB multilayer transferred at subphase pH 5.0.

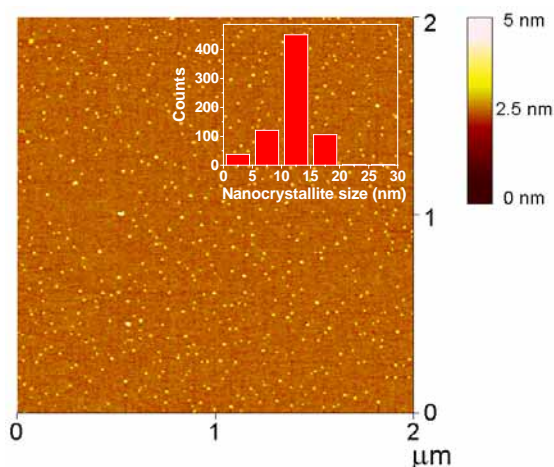


Fig. 2. AFM image of ZnO nanocrystallites obtained by oxidation at 700°C of a 7-monolayer ZnA LB multilayer transferred on mica substrate at subphase pH value of 5.0.