ZnO films can be electrodeposited cathodically from aqueous zinc salt solutions in the presence of oxidants like O₂ [1]. The electrodeposition of nanoporous ZnO was first demonstrated by addition of water-soluble organic dye molecules with anionic groups such as –SO₃⁻ or – COO⁻, which adsorb on the growing ZnO surface, to the electrodeposition bath [2]. More recently, addition of amphiphilic molecules with anionic groups such as sodium dodecyl sulfate was also found to lead to the formation of porous ZnO [3,4]. A lamellar structure with alternating layers of ZnO and amphiphilic molecules was reported for films electrodeposited in the presence of surfactants like sodium dodecyl sulfate, alkyl phosphates and alkyl sulfonates [3].

In general, a detailed understanding of the micelle formation, which occurs above a critical micelle concentration (cmc), is crucial for the preparation of porous materials by use of surfactants. Typically cmc values reported in the literature were obtained from concentration dependent conductivity measurements at room temperature in pure solvent. However, elevated temperatures and high concentrations of foreign ions as used in the electrodeposition of ZnO are expected to change the cmc.

In this study, we determined the cmc values for several alkyl sulfates and alkyl sulfonates with different chain lengths directly in the electrodeposition bath by surface tension measurements. The cmc values were found to be significantly lower under electrodeposition conditions compared to the cmc in pure water at room temperature. Subsequently, we performed electrodeposition of ZnO films in the presence of surfactant concentrations both above and below the cmc in order to elucidate the influence of the micelle formation on the structure and porosity of the deposited films.

Two ZnO phases were formed during the surfactant-assisted ZnO electrodeposition depending on the surfactant concentration. The already known [3] lamellar ZnO phase with alternating layers of ZnO and surfactants (Figure 1) was found only for surfactant concentrations from above the cmc down to about half the cmc. Since surface micelles are known to form at concentrations down to about half the cmc, the formation of micelles or surface micelles is thereby proven to be essential for the formation of the lamellar phase. The formation of the surfactant layers can thus be regarded as a “flattening” of surface micelles or the combination of several surfactant micelles. The presence of the surfactant layers in the as-deposited films is proven by the detection in energy-dispersive X-ray spectrometry (EDXS).

A second, hitherto unknown nanoparticulate ZnO phase with nanocrystallites of about 20 to 50 nm size (Figure 1b) was found at surfactant concentrations below the cmc. At concentrations well below the cmc, where no surface micelles are formed, only the nanoparticulate phase is formed. In comparison with ZnO deposited in the absence of surfactant molecules, in which ZnO columns with lengths in the µm-regime and diameters of 200-300 nm are formed, the almost spherical ZnO particles of the nanoparticulate phase are surprisingly small. In order to explain this remarkable result it can be assumed that an adsorption of the surfactant molecules on the surface of the ZnO particles blocks their growth. Since the molecules only reversibly adsorb to the surface, no sulfur from the sulfates or sulfonates was detected in the deposited films by EDXS measurements.

The results confirm that the critical micelle concentration and therefore the molecular assembly of surfactant molecules at the ZnO surface play an important role for the texturing of electrodeposited ZnO films. Furthermore, it is shown that the cmc is strongly influenced by the temperature and ionic strength of the electrodeposition bath. Consequently, it is essential to measure the cmc directly in the electrodeposition bath under deposition conditions.

References