From ZnO Colloids to Nanocrystalline Colored $Zn_xTi_{1-x}O_yN_z$ - Spinel Films

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This contribution highlights our efforts to elaborate new semiconductor nanostructures for solar technologies. Of particular interest to us at present are the colored powders and layers of zinc- and titanium oxynitrides. The last one has been demonstrated to be photoactive in the visible wavelength range. In order to get colored oxynitrides, one can perform an ammonia induced replacement of oxygen by nitrogen according to the general equation

$$M_xO_{2y} + 2z\,NH_3 \rightarrow M_xO_{(2y-3z)}N_{2z} + 3z\,H_2O$$

well known from the classical solid state chemistry.

Our new low cost colloidal sol-gel route to nanosized colored $Zn_xTi_{1-x}O_yN_z$ powders and porous layers on glass proceeds as follows. We firstly prepare alcoholic ZnO nanocolloids containing hexagonal Wurtzite particles with sizes around 5 nm. To the fresh sols, we add titanium tetraisopropoxide (Zn/Ti = 1) which readily reacts with the ZnO nanocrystals. During this interfacial reaction, the ZnO optical absorption spectra experience a blue-shift. The wet films prepared from these Ti^{4+}-functionalized ZnO sols via dip coating of glass slides are than pre-sintered at 400°C in air to remove the organic residues. The resulting layers are then annealed under ammonia gas at temperatures between 500°C and 800°C.
Figure 1 shows changes in the optical transmission spectra of the films as function of the nitriding temperature.

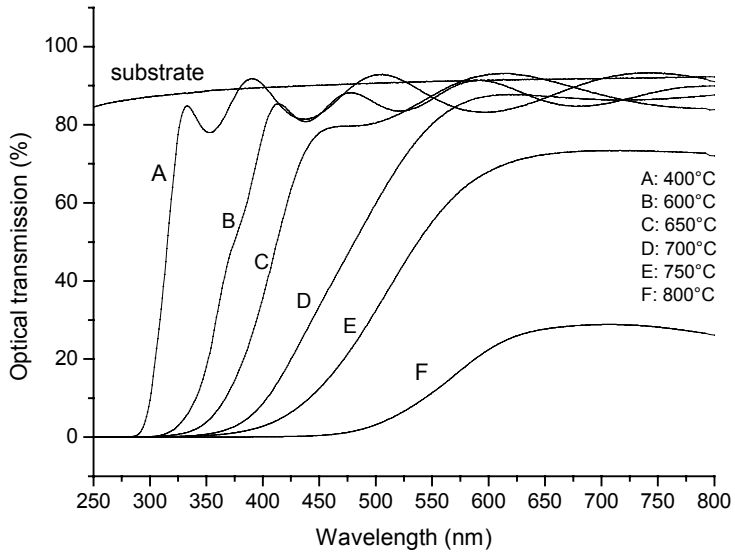

Fig. 1 Changes in the optical transmission spectra of "ZnTiON"-layers with increasing nitriding temperature

Above the dissociation temperature of ammonia (around 550°C), the spectra are progressively red-shifted with increasing nitriding temperature as it can be clearly recognized in Figure 1. The resulting layers show a high optical transparency as it is visually seen in Figure 2.

Fig. 2. Camera image of app. 1 µm thick $Zn_xTi_{1-x}O_yN_z$ films reflecting their high optical transparency and nitridation induced coloration. AFM-derived roughness values of the above films were determined to be of about 5 nm and the film thickness was of about 1 µm.

The results of our Electron Energy Loss Spectroscopic experiments (EELS) performed on a $Zn_xTi_{1-x}O_yN_z$ film are shown in Figure 3.

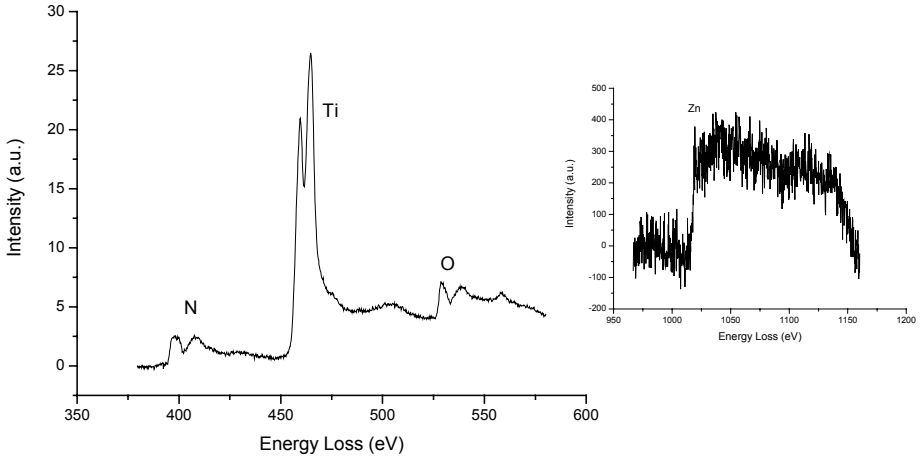

Fig. 6. EELS survey detected on a $Zn_xTi_{1-x}O_yN_z$ film obtained from 750°C nitriding experiment.

It proofs the presence of Zn, Ti, N and O atoms. The elastic peaks of the retro-diffused electrons are located at 458 eV (Ti L_{23}-edge), 396 eV (N K-edge), 530 eV (O) and at around 1020 eV (Zn). A detailed fine-structural XPS- and EELS-analysis of our $Zn_xTi_{1-x}O_yN_z$ nano-structures will be published elsewhere.

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