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ZnO nanostructures with a size ranging from 20 to 100 nm were successfully deposited on (1 0 0)-Si substrates at different temperatures (500–800 °C) using MOCVD. It could be confirmed that the size of ZnO nanostructures decreased with increasing growth temperature. From photoluminescence (PL) studies it was found, that intensive band-edge PL of ZnO nanostructures consists of emission lines with maxima at 368.6 nm, 370.1 nm, 373.7 nm, 383.9 nm, 391.7 nm, 400.7 nm and 412 nm. These lines can be dedicated to free excitons and impurity donor-bound excitons, where hydrogen acts as donor impurity with an activation energy of about 65 meV. A UV shift of the band-edge PL line with increasing growth temperature of ZnO nanostructures was observed as a result of the quantum confinement effect. The results suggest that an increase of growth temperature leads to increased band-edge PL intensity. Moreover, the ratio of band-edge PL intensity to green- (red-) band intensity also increases, indicating better crystalline quality of ZnO nanostructures with increasing growth temperature.