Study of nucleation and growth mechanisms for optimized and large-scale synthesis of aligned ZnO nanorods for photovoltaic applications.

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The growth of ordered ZnO nanostructures is very important for many application fields, as optoelectronics, photovoltaics, piezo-electric power generation, etc. In particular, vertically aligned ZnO nanorods can be employed as 3D electron-harvesting TCO, capable of inducing multiple absorptions by light scattering phenomena in hybrid third generation solar cells. However, for photovoltaic application it is necessary to produce large area substrates uniformly covered by nanorods with controlled dimensions.

Aligned ZnO nanorods can be obtained in highly ordered arrays over different substrates both by wet chemical methods and by vapour-phase processes. Not-catalyzed vapour growth processes are those that can supply nanostructures with the lowest concentration of undesired impurities. This aspect is fundamental for photovoltaic application in order to prevent negative effects on electron transport properties.

In this work, we report the preparation of a large area (few square centimetres) nanostructured TCO on commercial glass substrate, constituted by a highly conducting ZnO:Al layer (by Pulsed Electron Deposition) and vertically aligned ZnO nanorods homogeneous in length and diameter over the whole substrate. The latter have been obtained by a vapour-phase process, starting from metallic Zn where only argon and oxygen flows are used, with a maximum temperature lower than 500°C (which is compatible with low-cost and application-oriented glass substrates).

This goal has been achieved after an in-depth study of the nucleation and growth mechanisms of ZnO nanorods. The influence of substrate material and its crystallographic properties, as well as the results obtained with different growth parameters (temperature, flows, time) are discussed. Above all, it has been observed that the condensation of small Zn clusters on the polar surface of a ZnO film can reproducibly nucleate the growth of ZnO well-aligned rods, perpendicularly to the substrate face. These clusters can be formed by a proper control of temperature gradients in order to obtain locally a zinc vapour pressure larger than the equilibrium one of liquid phase.

Once nucleation has occurred, the growth of the nanorods follows until zinc and oxygen are supplied. Diameter of nanorods can thus be intentionally modified in the 20-200 nm range, and length up to 3-4 microns. Moreover, it has been evidenced that during the growth process a ZnO wetting layer of controllable thickness can be deposited between the ZnO:Al layer and nanorods.