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Polycrystalline titania and Nb:$TiO_2$ thin films were deposited by RF magnetron sputtering. The influence of post-deposition annealing in vacuum and hydrogen atmosphere on the structure, morphology, oxidation states and optical properties was studied by X-ray diffraction, atomic force microscopy, XPS and UV–VIS spectroscopy. The heat treatment of titanium dioxide thin films in vacuum and $H_2$ atmosphere induces structural and morphological changes. The band gap narrowing was observed for the transparent as-deposited Nb:$TiO_2$ films, while annealing at 420 °C in $H_2$ atmosphere resulted in an enhancement of the electrical conductivity. Further on, $TiO_2$/*p*-CdTe photovoltaic devices with efficiency of 1.8% were fabricated and their characteristic 'enhancement' is discussed.