Polycrystalline titania oxide are of great interest recently namely for their photocatalyical properties. In our contribution we will present structural studies of thin layers prepared on different substrates (amorphous glass and crystalline silicon) by dip-coating method. A set of layers were analysed all of them synthesized via sol-gel process controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane combined with pressurized water extraction and/or supercritical/pressurized methanol drying. Obtained thin films were heated up to 400°C for 4 hours in order to obtain crystalline phase. Samples have been analyzed using x-ray diffraction, x-ray reflectivity and x-ray fluorescence spectroscopy. The real structure of thin layers have been investigated using software package MStruct.