In this work, Ba0.8Sr0.2TiO3 (BST) films on LaNiO3-buffered SiO2/Si (LNO/SiO2/Si) substrates were crystallized by pulsed laser irradiation. Solution-derived amorphous barium–strontium–titanate precursor layers were crystallized with a KrF excimer laser in oxygen ambient at fluences ranging from 50 to 75 mJ cm−2. With the substrate temperature set to 500 °C, the number of pulses and film thickness were varied until high-quality crystallinity could be achieved. It was found that films with a thickness of 40 nm are fully crystallized with a uniaxial {001} orientation which is predetermined by the LaNiO3 orientation. On the other hand, for 160 nm thick films, crystallization was observed after 12,000 pulses in the 70 nm close to the surface, while the rest of the film remained amorphous. The large temperature difference between the film surface and interface due to the low thermal conductivity of the amorphous BST is suggested as the origin of this behavior. Films thicker than 80 nm cracked on crystallization due to the stress caused by the different thermal expansion coefficients of film and substrate, as well as the large temperature variations within the BST film.