The objective of the present study was to investigate whether analysis of carbon dioxide, acetone, and/or butanol present in human breath can be used as a simple and non-invasive diagnosis method for obstructive sleep apnea syndrome (OSAS). For this purpose, overnight changes in the concentrations of these breath molecules were measured before and after sleep in ten patients who underwent polysomnography and were diagnosed with OSAS, and were compared to the levels of these biomarkers determined after sleep in ten healthy subjects. The concentrations of exhaled carbon dioxide were measured using external cavity laser (ECL)-based off-axis cavity enhanced absorption spectroscopy (OA-CEAS), whereas the levels of exhaled acetone and butanol were determined using thermal desorption gas chromatography mass spectrometry (TD-GCMS). We observed no significant changes in the levels of exhaled acetone and carbon dioxide in OSAS patients after sleep compared to pre-sleep values and compared to those in healthy control subjects. However, for the first time, to our knowledge, analyses of expired air showed an increased concentration of butanol after sleep compared to that before sleep and compared to that in healthy subjects. These results suggest that butanol can be established as a potential biomarker to enable the convenient and non-invasive diagnosis of OSAS in the future.