Attention-deficit hyperactivity disorder (ADHD) is characterized by deficits in executive functions and decision making during childhood and adolescence. Contradictory results exist whether altered event-related potentials (ERPs) in adults are associated with the tendency of ADHD patients towards risky behavior. Clinically diagnosed ADHD patients (n = 18) and healthy controls (n = 18), aged between 18 and 29 (median 22 Yo), were screened with the Conners’ Adult ADHD Rating Scales and assessed by the Mini-International Neuropsychiatric Interview, adult ADHD Self-Report Scale, and by the 60-item HEXACO Personality Inventory. The characteristic personality traits of ADHD patients were the high level of impulsiveness associated with lower values of agreeableness. All participants performed a probability gambling task (PGT) with two frequencies of the feedback information of the outcome. For each trial, ERPs were triggered by the self-paced trial onset and by the gamble selection. After trial onset, the latency of the N2-P3a ERP component associated with the attentional load was shorter in the ADHD group than in controls. An N500 component related to the feedback frequency condition after trial onset and an N400-like component after gamble selection suggest a large affective stake of the decision making and an emphasized postdecisional evaluation of the choice made by the ADHD participants. By combining ERPs, related to the emotions associated with the feedback frequency condition, and behavioral analyses during completion of PGT, this study provides new findings on the neural dynamics that differentiate controls and young ADHD adults. In the patients’ group, we raise the hypothesis that the activity of frontocentral and centroparietal neural circuits drive the decision-making processes dictated by an impaired cognitive workload followed by the build-up of large emotional feelings generated by the conflict towards the outcome of the gambling choice. Our results can be used for new investigations aimed at studying the fine spatiotemporal distribution of cortical activity, and the neural circuits that underly the generation of that activity, associated with the behavioral deficits characteristic of ADHD.