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Organic light emitting devices (OLEDs) have been attracting considerable interests since its application on flat panel display. The development of OLED can be achieved by the effective surface interface analysis using photoelectron spectroscopy (PES) technique. In this report, we present the effective analysis techniques showing the electronic structures of OLED interfaces with essential information on the mechanism of OLED. The surface interfaces in OLED have been probed with the PES in order to reveal the nature of physical phenomena occurring on sandwiched interlayers between a cathode and Alq3 layer. The device characteristics and the interface electronic structures of OLED based on Alq3 is to be presented with Al/CaF₂, Al/MgF₂, Al/LiF and Al only cathodes.