Abstract: Polyethylene (PE) samples were surface fluorinated by the F<sub>2</sub>/N<sub>2</sub> mixture for 30, 60, 120 or 240 min to investigate the influence of the fluorinated layer characteristics on space charge accumulation. After polarization at 50 kV mm<sup>-1</sup> dc electrical field and 40 °C for 240 min, the charge amounts of the samples fluorinated for the different times, normalized to the charge amount of the original sample, are 1.17, 0.51, 0.49 and 0.22, respectively, showing significant suppression of the charge accumulation by the longer treatments, especially for the 240 min treatment. Infrared analyses and SEM cross-section images of the fluorinated samples indicate the increases in degree of fluorination and thicknesses of the fluorinated layer with the treatment time, and the fluorinated layer thicknesses were determined to be 0.39, 0.45, 0.65 and  $0.80 \mu m$ . Surface energy calculations show that the polar component increased from 2.9 to 14.7 mJ m<sup>-2</sup> after the 30 min treatment, and subsequently decreased to 11.8, 11.5 and 9.5 mJ m<sup>-2</sup> for the longer treatments of 60, 120 and 240 min. This suggests a similar change in surface layer permittivity with the treatment time. The fluorinations led to the shift of thermally stimulated discharge current peak from 156 °C of the original sample to 145, 142, 144 and 149 °C of the fluorinated samples, and thus reduced the trap depth of the surface layer. But, the longer treatments of 60, 120 and 240 min significantly improved the barrier properties of the surface layer to the diffusion of the chemical species from the semi-conductive electrode to the PE by the decrease in free volume of the surface layer. The chemical species diffused into the sample surface layer reduced the depth of surface traps. The decrease in free volume is more important in suppressing the charge accumulation than the increase in surface layer permittivity and the change in surface trap, because it would reduce the charge transport in the surface layer and the charge direct injection at both electrodes.