The impact of thin organic films on the barrier heights of Ag/n-GaAs(0 0 1) Schottky contacts is investigated using complementary experimental and theoretical techniques, namely current–voltage (I–V) measurements, impedance spectroscopy, and internal photoemission spectroscopy, as well as drift diffusion simulations. The in situ current–voltage characteristics show that the effective barrier height decreases by ~200 meV as a function of the 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) layer thickness. The effects responsible for the decrease in barrier height are derived from calculations using a two-dimensional drift-diffusion simulator. The simulations show that image force lowering is responsible for the decrease in barrier height. Upon air exposure barrier heights of organic modified contacts are found to increase reaching values which are higher than the ones for the unmodified contacts. Internal photoemission spectroscopy investigations show that the properties of organic/GaAs(1 0 0) interface is not modified by the exposure to air. Therefore, the increase in barrier height is due the contamination of the PTCDA/Ag interfaces resulting in interface states. Due to these interface states the Fermi level shifts by about 0.2 eV.