In this work, we studied the effect of RbF post-deposition treatment (PDT) on Cu(In,Ga)Se₂ (CIGS) by investigating the surface chemistry, morphologies and improve device performance of CIGS thin film solar cells on flexible polyimide substrates. The absorber films were formed by three-stage co-evaporation and RbF treatment was followed for 10 min. We examine the solar device parameters and observe a positive trend in the polarization curve when moving from devices from without PDT to NaF-, KF-, and RbF-PDT. Also, dual-PDT was carried out by depositing KF or RbF after NaF treatment. Rb-treated CIGS films were characterized by various analytical methods including electron microscopy Kelvin probe force microscopy, and atom probe tomography. The introduction of Rb into CIGS layer appears to induce a sharper p-n junction with CdS buffer layer by keeping the lower Cu concentration at the surface, which is expected to bring a positive contribution to open-circuit voltage, fill-factor, and therefore power conversion efficiency. An improved device performance with RbF-PDT was achieved compared to pristine CIGs solar cells, which shows the potential of fabrication highly-efficient flexible CIGS solar cells.