At BESSY-II ellipsometric techniques have been established as a sensitive probe to characterize and model multilayer optical systems for the EUV- and XUV range, operated in reflection and transmission. The reflection and transmission coefficients Rs and Rp (Ts, Tp, respectively) and their relative phase $\Delta s-p$ is obtainable with a high precision. As a spin-off precise information about the polarization state of the undulator radiation is extracted. This technique is demonstrated for the case of a reflective Mo/Si multilayer system for EUV lithography application. It is shown that there is considerable phase mismatch between waves reflected in s- and p-geometry even in near-normal incidence application. In the range of the Brewster angle the Bragg reflection curves and their peak positions are strongly modulated by the polarization of the incident beam. The existing polarimetry instrumentation and our upgrade program for at-wavelength metrology on real-size reflection gratings on a new VUV and XUV Optics beamline which will go into operation by the end of this year will be shown.