Ellipsometry is a non-destructive and indirect technique able to characterize optical and electrical properties of thin films and bulks, besides determining the thickness of thin films. This characterization is performed by evaluating the change in polarization state of light when it interacts with the material of interest. In this work the ellipsometry technique was used to characterize the optical and electrical properties of AZ31 magnesium alloy samples. This alloy has several interesting properties such as high thermal conductivity, good machinability, among others, which makes it suitable for use in automotive and aerospace components, for example. When exposed to ambient atmosphere, this alloy undergoes naturally oxidation, developing a surface layer of oxides. Thus, this study aimed to establish an efficient methodology for accessing the optical and electrical characteristics of the substrate (AZ31 alloy) as well as those for the surface layer of oxides, and to obtain the thickness of this layer. From the results of the ellipsometric measures and the appropriate modeling, it was possible to determine the refractive index (n) and extinction coefficient (k) curves versus wavelength for the substrate (AZ31 alloy), as well as for the oxide layer, plus the thickness of the latter.