The quantization of electronic states in thin metallic films is now well-established, having been observed in a number of systems including films on metal as well as semiconductor substrates. The impact of this quantization on the films’ physical properties has been demonstrated in several studies, including the dependence on thickness of films’ thermal stabilities, work functions, and superconductivity transition temperatures. In the simplest model, the electrons are confined to the film by the substrate and vacuum interfaces, which work as “mirrors” to reflect the electrons back into the film, resulting in discrete standing-wave states. In this picture, the substrate forms a reflecting barrier due to a mismatch of electronic structures between it and the overlayer, and the main result is the formation of discrete energy subbands. In this talk, photoemission results will be presented from a variety of thin-film systems that show more interesting electronic structures due to interactions with the substrate and interface. The systems studied highlight different effects, including interfacial scattering and diffraction, hybridization of film and substrate states, and the formation of a composite quantum well from a thin metallic film on a semiconductor. In the latter case, the semiconductor depletion region forms part of the system via coherent coupling between film and substrate electronic states. In collaboration with S. J. Tang, N. J. Speer, D. Ricci, M. Upton, L. Basile, S.-L. Chang, Y.-R. Lee, and T.-C. Chiang.