The nature of the contact material plays a key role to determine the characteristics of electrical arcs and particularly those related to electronic emission. Mechanical and thermodynamic properties as well as electronic emission of such complicated alloys present a lack of reliable and accurate experimental data. The purpose of this paper is to present the development of a method for measuring photoelectric work functions of contact materials. Also reported in this paper are the results of experimental work whose purpose has been the buildup of a reliable photoelectric system and associated monochromatic ultraviolet radiations source, and the photoelectric measurement of the EWF of contact materials. As a first test of the experimental Ultra High Vacuum setup, the electron work functions (EWF) of silver contacts, namely pure polycrystalline metals that are actually used in relays, were measured photoelectrically, using both Fowler's method of isothermal curves and linearized Fowler plots. Ultrahigh vacuum techniques were employed to obtain residual gas pressure of about 5×10−9 mbar that allows accurate and reliable photoelectric work function measurements. The EWF measured at room temperature of polycrystalline Ag contact (as commercially available) increased from 3.70 eV before heating, to 4.30 eV, and finally, stabilized at the vicinity of 4.26 eV after several vacuum heat treatments at 533 and 773 K. The EWF value obtained, i.e., 4.26 ± 0.03 eV, is in good agreement with the results found in the literature. This shows that the experimental method is valid and the experimental setup is usable. Furthermore, new photoelectric measurements versus temperature have shown a linear decrease of the EWF of silver contacts with increasing temperature, i.e., the temperature coefficient $\alpha = d\phi/dt$ is constant and negative $\alpha = -4.58 \cdot 10-4$ eV/K in the experiment temperature range 300–780 K