

ABSTRACT

This thesis concerns the preparation and characterisation of ultra-thin films of alkali metals (AM) deposited onto highly oriented pyrolytic graphite. The main probe is photoemission in the near UV range where valence- and shallow AM core level electrons can be studied. During the course of the work it was found that also an emission line due to an empty state in graphite, populated by secondary electrons, is useful for monitoring the initial stages of growth. The motivation for the work was that AM films on graphite should realize simple metal quantum wells in which all valence electrons are confined and therefore found in a ladder of discrete levels. The confinement is restricted to electron energies and parallel wave vectors within a substrate band gap and for previously studied systems this has meant that only a modest fraction of the valence electrons can form discrete states.

After experimenting with the preparation procedure it is found that Na films may be grown nearly layer by atomic layer. The three-dimensional growth noted in previous work can be avoided by evaporation at 40 K followed by annealing at around 90 K. From the level energies recorded for 1-15 ML thick films the dispersion of Na valence electrons in the range 0-1.5 eV below E_F is found to be close to free electron like and indicating a 110-oriented film, which is confirmed by STM observations for films thicker than 2 ML. The 1.5 eV energy range for which the dispersion is determined corresponds to around half of the filled band width of Na. This limit is not set by the substrate band gap but by the level separation becoming smaller than the lifetime width of the emission lines. A strong oscillatory photon energy dependence is observed for the cross section of quantum well states similar to that observed previously for Na/Cu(111).

For the AM studied (Na, K, Rb, and Cs) there exists a dispersed phase at low coverage but an onset of condensation occurs in the submonolayer coverage range. For Na the states in Na islands can be detected via a quantum well state down to 1% surface coverage. The island formation observed at 90 K can be monitored in real time. For all the AM the initial growth can be monitored via a coverage dependent shift and splitting of a graphite secondary line. The shift is linear with the work function change. Based on the observed atomic size dependence it is suggested that one may extract the location above the graphite surface of the screening charge below an adsorbed AM atom. As the coverage of K, Rb, or Cs is increased and condensation occurs the secondary line shows a stepwise energy shift and a strong intensity increase to a maximum reached at full monolayer coverage but for Na none of this is observed. The interpretation suggested for this striking difference is that the shifted peak results from diffraction by a (2×2) ordered AM layer. This order is common for the heavier AM but not expected for Na.

Based in part by the unusual behavior of the secondary line for K another interpretation of the K data was first suggested, namely that the initial formed K condensate is intercalated. Due to uncertainty about this suggestion the data base was extended to high photon energies and these results are in favor of an interpretation of an adsorbed K condensate. Some of the high photon energy spectra were recorded with light of high intensity and this was found, via the K $3p$ emission, to induce changes of the sample which are not understood but are not due to desorption.

Keywords: Angle resolved photoemission, Quantum well states, Ultra thin overlayers, Alkali metal, Graphite, Phase transition.