A First-Principles Study of Interface Systems: Electronic properties of Metal Quantum Wells and Varistor Materials.

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Abstract

This thesis [1] focus on the effects of electron localization in an alkali monolayer on a metal surface and at grain boundaries in varistor materials. The *first-principles* calculations confirm the existence of a quantum well state, quasi localized in the Na monolayer adsorbed on the Cu(111)-surface, which has previously been observed by photoemission experiments. The calculated coverage dependence, dispersion of the quantum well band and the calculated vibration frequency for the perpendicular mode of the Na adlayer agrees with experimental results. Calculations also indicate that the electron-phonon interaction in the Na monolayer gives the main contribution to the lifetime broadening of the photoemission peak of the electron extracted from the quantum well band.

The non-linearity of the ZnO based varistors is connected to the properties of the grain boundaries in the materials. Simulations of the I-V characteristics indicate that disorder in the material degrades the non-linearity of the varistor. Calculations of the microscopic properties of the varistor materials show that neither the polar {0001}-surfaces nor the Σ=13 tilt grain boundary in ZnO have any acceptor states with energy levels in the band gap. The broken bonds at the polar surfaces rather have the tendency to compensate the fields in the crystal.

Mixing ZnO and Bi_2O_3 leads to a phase separation because the formation energies are large for both the Bi-impurity in ZnO and for the Zn-impurity and the Bi-vacancy in Bi_2O_3. The formation energy for Sb- and Bi-impurities in the Σ=13 tilt grain boundary were much lower, which suggests that these impurities would remain in the grain boundary region after the liquid sintering step in the varistor manufacturing process. These results are consistent with the experimental observations of high concentrations of Bi_2O_3 and $Zn_7Sb_2O_{12}$-phases in the grain boundary region in varistor materials.

The Sb- and Bi-impurities in ZnO act as donors at low impurity concentration, but a localized Bi-Bi σ-bond is formed at higher Bi-concentration in the grain boundary. This Bi-Bi state is located in the band gap of ZnO and it is therefore possible to manipulate its population by an external field. The occupation and depletion of this Bi-Bi state could then be responsible for the varistor effect observed in Bi-decorated grain boundaries.

The Bi-vacancy in $\alpha - Bi_2O_3$ in addition gives rise to an acceptor state in the bandgap. Although the formation energy for this vacancy in the bulk material is high, it is probable that the less ordered Bi_2O_3-phase between the grains contains a considerable amount of Bi-vacancies. The Bi_2O_3-phases that cover the ZnO grains could then be the host of the acceptor states which are responsible for the formation of the Double Schottky Barrier in Bi-doped ZnO varistors.

[1] **Keywords:** Metallic quantum wells, metal oxides and varistors, surfaces, grain boundaries and impurities, Density functional calculations.