Classical and semiclassical approaches for determination of the intergranular energy barrier height in metal-oxide nanograins

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Since pioneering modeling by Schottky and Bardeen, a deep insight into the comprehension of the nature of a semiconductor-metal junction has been addressed. Such knowledge is the base of the working mechanism of gas sensing via chemo-resistive metal oxides. The advent of nanostructures has pursued this study still further due to significant change in the surface parameters with respect to their coarser-grained counterparts. The height of the inter-grain energy barrier plays key role in the determination of the conductive properties of semiconducting nanograins.

We firstly approached the calculation of the inter-grain energy barrier for a nano-structured semiconductor under pure classical conditions. A model for Schottky contacts to be applied to nanosized polycrystalline *n*-type semiconductors was developed. To this purpose we determined the density of surface states as a function of the mean grain radius, which establishes the Schottky barrier height. The intergranular potential shape was investigated in depletion approximation under spherical geometry with a critical revision of the condition for which such an approximation is valid. It was demonstrated that for very small grains the depletion approximation cannot be applied, and Poisson equation must be solved with the complete expression for the charge density. Here some effects due to low-grain dimensionality come out, such as the effect of band flattening.

With the depletion length of the order of the grain size, a significant role in a sensor's response owes to the effect of Fermi level pinning, which removes the linear relationship between the work function and the Schottky barrier. We discuss the conditions under which pinning plays a role or it does not.

Indeed, as the grain size becomes sufficiently small, quantum effects start playing non-negligible role. Quantum effects are hard to be taken into account mostly for the difficulty in applying *ab initio* approaches to such a multi-particle system as a nanograin. In the limit of ultra-fine nanograins (of the order of 1 nm), quantum effects start being relevant in the determination of the properties. We propose a model working within a range of grain size that cannot be treated in a purely classical way, i.e., on the border region where quantum confinement starts being effective. We approached the problem in a semi-classical method through the Thomas-Fermi equation. In particular we calculate the inter-granular energy barrier in metal-oxide chemoresistive materials and compared theoretical expectations to experimental results.

A comparison between models and experimental evidences is given and future possibilities for modeling of very- and ultra-fine grains are highlighted.