## LA01

## LOCALIZED 3d STATES IN SPINTRONIC MATERIALS – STUDIES WITH USE OF SYNCHROTRON RADIATION

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In common semiconductors, like CdTe or GaAs, fully occupied cation d states occur a few electronvolt below the valence band. They can influence a little the position of the bands lying above them but contribute very weakly to the density of states of those bands. Therefore, they are frequently considered as core levels.

However, the role of open (partly occupied) d shells in solids containing transition metal atoms is much more important. This shell contributes markedly to the valence band and determines the magnetic properties of the crystal. In such materials d states are still relatively localized, however, their energy position is close to the position of valence orbitals forming the band structure of the crystal. So, the properties of the system strongly depend on the relative strength of two competing factors: intra-shell correlation effects and interaction between dstates and the electronic states of neighbouring atoms.

Importance of the open d shells manifests itself particularly clearly in diluted magnetic semiconductors (DMS) [1]. Magnetic moments of Mn ions derived from magnetic properties of DMS correspond to moments of intact d shell. However, the strong coupling between magnetic and optical or transport properties shows that *s*,*p*-*d* hybridisation is not negligible in these systems. Thus, both intra-shell correlation and interaction with neighbours have to be taken into consideration.

Recently emerging idea of spin-based electronics (spintronics) [2] increased the importance of DMSs and related materials. In particular, ferromagnetic semiconductors attract great interest. Such materials would be necessary for fabrication of spintronic devices in which spins of electrons can be manipulated with electric field or light. GaMnAs became the most intensively studied material of this family, due to relatively high Curie temperature. It is usually grown by means of low-temperature MBE, in order to increase the amount of Mn (very low for equilibrium growth methods). The proper post-growth treatment leads to increase of the Curie temperature to about 160 K [3]. So, the search for new ferromagnetic materials with Curie temperature higher than room temperature is still in course. Knowledge of the charge state of Mn ions and energy distribution of Mn *3d* states is important for it.

In the lecture, the investigations of an interesting example of such a compound - manganese arsenide – will be considered.

Thin layers of MnAs grown on various substrates attract considerable interest due to coupling between their structural characteristics and ferromagnetic properties at room temperature. In this paper we report a successful growth of MnAs layers on GaN(000<u>1</u>)-(1×1) surface as well as a study of their morphology, electronic structure and magnetic properties. Both materials have hexagonal structures in the plane perpendicular to the *c* axis but  $a_{MnAs}>a_{GaN}$ . As a consequence, formation of MnAs dots in this system can be expected (in contrast to, for example, MnAs/GaAs(111) system). The layers of MnAs were deposited stepwise by an MBE technique. Their structure was assessed by RHEED and LEED techniques.

The first steps of deposition (1 - 2 ML) caused blurring of the streaked pattern of GaN(000<u>1</u>)-(1×1). Further deposition led to improvement of the pattern (streaks became again stronger and sharper) then, at about 7 ML, the critical thickness was achieved and a dotted pattern (characteristic of 3D growth) appeared. An *ex situ* AFM investigation of the surface morphology of the 8-10 ML-thick layers proved that MnAs formed grains of the diameter 20-60 nm and of the average height of 4 nm. Ferromagnetic properties of the system were revealed by SQUID. The Curie temperature was about 270 K.

The electronic structure of MnAs was investigated *in situ*, at each stage of growth, by means of resonant photoemission spectroscopy, for photon energies close to Mn3*p*-3*d* transition. Thus, features of this experimental method, very useful for investigation of open-shell contribution to the electronic structure of solids, will be exemplified through the results acquired for MnAs.



Figure 1. Scheme of a resonant photoemission process far a Mn ion. Quantum interference between two final states leads to a Fano effect.

The resonant photoemission spectroscopy is based on the Fano effect occurring when a discrete energy state interferes with a continuum state of the system [4]. Then, an asymmetric line shape (the Fano profile) appears in the transition probability. For manganese atoms the following processes are considered (Fig. 1):

> Mn  $3p^63d^5 + hv \rightarrow Mn 3p^63d^4 + e^-$ (transition to the continuum state)

> and Mn  $3p^63d^5 + hv \rightarrow Mn 3p^53d^6$  (transition to the discrete state).

Thus, the Fano effect leads to an enhancement of photoemission from the Mn 3*d* shell. As a consequence, resonant photoemission can be used for identification of the features in the photoemission spectra which can be ascribed to the emission from that partly filled shell. Figure 2 shows the map of intensity of photoemission from the MnAs(10 ML)/GaN system. A marked increase of emission occurs for the photon energy of 52 eV. This photon energy corresponds well to the energy of Mn 3*p*-3*d* transition. A comparison of the spectrum taken for the resonance energy with that measured for the anti-resonance energy (corresponding to the minimum of the Fano profile – about 47 eV for MnAs/GaN) allows revealing of the Mn 3*d* cotribution to the electronic structure of the system.



Figure 2. Photoemission intensity as a function of the binding energy and photon energy. The binding energy range covers the valence band and Ga 3d level. Maximum emission in the valence band clearly seen for the photon energy of 52 eV.

So, the Mn 3d contribution to the spectra (covering the whole valence band, with maximum at about 4 eV below the Fermi energy) was determined for MnAs/GaN. Its shape was compared with those observed for pure Mn deposited on GaN surface and from GaMn. The substantial differences confirmed that the electronic structure of MnAs was revealed.

A necessary condition for carrying out resonant photomission experiments is accesses to a tunable source of hard ultraviolet radiation.

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