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VALENCE BAND DENSITY OF STATES AND Mn 3*d* CONTRIBUTION IN $\mathrm{Mn}_{1-x}\mathrm{Mg}_x\mathrm{Te}$

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Resonant photoemission spectroscopy was applied to determine the Mn 3*d* derived contribution to the valence band density of states of $\mathrm{Mn}_{0.44}\mathrm{Mg}_{0.56}\mathrm{Te}$ grown by molecular beam epitaxy on a GaAs(001) substrate. The modifications of the valence band density-of-states distribution are discussed as a consequence of the substitution of Mg ions for Mn ions.

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1. Introduction

The group of Mg-based semiconductors has attracted an increasing interest since their importance as optoelectronic materials was demonstrated [1–3]. $\mathrm{Mn}_{1-x}\mathrm{Mg}_x\mathrm{Te}$, very recently grown by molecular beam epitaxy (MBE), is not an exception [4]. Moreover, due to the presence of Mn ions, it is expected to be a suitable material for magnetic barriers in quantum heterostructures. Therefore, it became a very interesting subject of studies carried out by means of different experimental techniques [4]. In particular, its band structure is far from being determined.

We present the results of photoemission studies undertaken in order to determine the valence band density-of-states (DOS) distribution in zinc blende $\mathrm{Mn}_{0.44}\mathrm{Mg}_{0.56}\mathrm{Te}$. The experiments were performed by means of resonant photoemission spectroscopy. This means that photoemission spectra were recorded for the photon energies close to the intra-ion Mn $3p^6 3d^5 \rightarrow$ Mn $3p^5 3d^6$ transition. The autoionization of the excited state to the Mn $3p^6 3d^4 + \mathrm{e}^-$ configuration (by the super Coster–Kronig decay) [5, 6] leads to the strong resonant enhancement of the spectral features corresponding to the emission from the Mn 3*d* shell. As the dependence of the resonant photoemission intensity is described by the Fano profile [5], the difference between the spectra taken on resonance and at antiresonance photon energy is interpreted as a measure of the Mn $3d$ contribution to the valence band. On the other hand, the comparison of the spectra with those previously collected for zinc blende (zb) MnTe [7], under the same experimental conditions, enabled us to identify other modifications of the valence band structure caused by the presence of Mg atoms.

2. Experimental conditions

The $Mn_{0.44}Mg_{0.56}Te$ layers were grown by an MBE technique on a GaAs(001) substrate with a CdTe buffer of the thickness of 1000 Å [4]. As the $Mn_{0.44}Mg_{0.56}Te$ layer thickness amounted to 2 μm we believe that the obtained results are representative for the bulk properties of the studied material. The clean surface for the photoemission experiments was prepared by Ar^+ ion sputtering (at the argon pressure of 1×10^{-4} torr and with the accelerating potential difference of 600 V) and annealing at 260°C under ultrahigh vacuum (UHV) conditions.

The experiments were carried out at the E1 beamline of the storage ring DORIS III in the synchrotron radiation laboratory HASYLAB in Hamburg, Germany. The FLIPPER II experimental setup, designed for sample preparation and extended characterization of solids by means of electron spectroscopies, was attached to the beamline via a plane grating monochromator which operated within the photon energy range of 15–200 eV [8].

3. Experimental results and discussion

Figure 1 shows the set of photoemission spectra acquired for the photon energies close to the energy of the Mn $3p \rightarrow 3d$ transition. The strong changes in the intensity of the peak at the binding energy of 4.5 eV, observed with the increase in photon energy, enabled us to determine the resonance and antiresonance photon energy as equal to 51.2 and 48.6 eV, respectively. The shape of the spectrum taken at the antiresonance energy is determined mainly by the distribution of the states constituting the valence band of the host semiconductor. A comparison of the antiresonance spectra of $Mn_{0.44}Mg_{0.56}Te$ and zb-MnTe (Fig. 2) shows that a substantial part of the valence band states was transferred to the deeper part of the band. It might be a manifestation of an interaction between the hybridised Mg $3s$, $3p$ and Te $5s$, $5p$ states. It can also occur due to the reduction of the number of Mn $3d$ states hybridising with the valence band states. However, it is difficult to propose a final interpretation before the results of band structure calculations are available.

In order to visualise the Mn-derived contribution to the valence band we subtracted the spectrum taken at the energy of 48.6 eV (antiresonance) from that obtained for $\hbar\nu = 51.2$ eV (resonance) (Fig. 2). The overall shape of the difference spectrum corresponds well to those obtained for Mn-based diluted magnetic semiconductors (DMS) [9, 10] and cubic MnTe [7, 11]. However, the relative intensities of its main components markedly differ from those reported for MnTe.

In the resonant photoemission difference spectrum of an Mn-based compound three main parts can be distinguished [9]. First of them (VB) corresponds to the upper part of the valence band, second one (M) is dominated by the main maximum of the difference spectrum at about 3.5 eV below the valence band edge

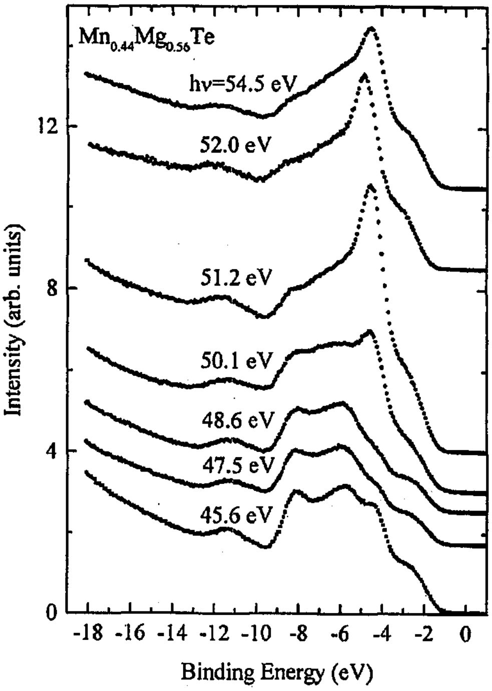

Fig. 1. A series of valence band spectra of $Mn_{0.44}Mg_{0.56}Te$ taken for photon energies near the Mn $3p \rightarrow 3d$ transition.

and the third component, the satellite (S), extends from the energy of about 6 eV to about 12 eV below the valence band edge. These three features are built of components corresponding to the emission processes which leave behind the Mn ion in final states belonging to two categories: d^4 and $d^5\underline{L}$. d^4 denotes the states with an unscreened hole in the Mn $3d$ shell. $d^5\underline{L}$ describes the states with the hole screened by the charge transfer from the ligands. The former states dominate the satellite structure and contribute to the main maximum. The latter states form the valence band part, dominate the main maximum and contribute to some extent to the satellite.

It was shown by means of configuration interaction (CI) cluster model calculations done for several Mn-based diluted magnetic semiconductors [8, 9] that the relative intensities ($I_{\mathrm{VB}}/I_{\mathrm{M}}$ and $I_{\mathrm{S}}/I_{\mathrm{M}}$) of the main parts of the resonant photoemission difference spectrum can be correlated with the energy position of Mn $3d$ states with respect to the anion p states composing the valence band as well as with the strength of the p–d hybridization. Therefore, our results could be interpreted as a symptom of the change in the strength of p–d hybridization, occurring due to the presence of Mg atoms. However, it was usually observed that an increase in $I_{\mathrm{VB}}/I_{\mathrm{M}}$ correlates with a decrease in $I_{\mathrm{S}}/I_{\mathrm{M}}$ and vice versa. It was also confirmed by CI cluster model calculations [9]. Comparing the difference spectrum of $Mn_{0.44}Mg_{0.56}Te$ with that of MnTe [7] we found that the values for both

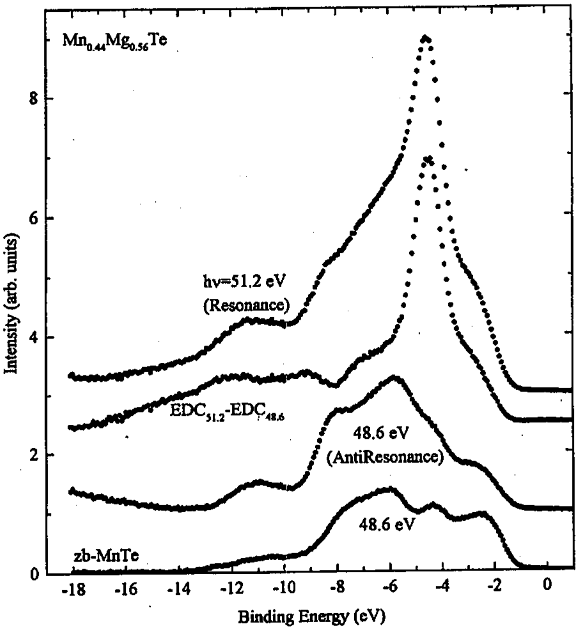

Fig. 2. The resonant photoemission difference spectrum of $Mn_{0.44}Mg_{0.56}Te$ obtained by subtraction of the curve taken at 48.6 eV (antiresonance) from that recorded for 51.2 eV (resonance) photon energy. The spectrum taken at the antiresonance photon energy for zb-MnTe is also shown.

I_{VB}/I_M and I_S/I_M are lower for $Mn_{0.44}Mg_{0.56}Te$ ($I_{VB}/I_M = 0.17$, $I_S/I_M = 0.27$) than for MnTe ($I_{VB}/I_M = 0.21$, $I_S/I_M = 0.54$). It suggests that not only the $d^5\underline{L}$ component has decreased in the whole difference spectrum. It seems that the transition probability distribution between ^5E and $^5T_2$ final states as well as the energy position of these states have been markedly modified.

The influence of the Mn contents on the shape of resonant photoemission spectra observed for $Mn_{0.44}Mg_{0.56}Te$ and MnTe contrasts with the results of photoemission studies of $Cd_{1-x}Mn_xX$ (X = S, Se, Te) [9], MnY (Y = S, Se, Te) (with NiAs-type or NaCl-type crystal structures, respectively) [12] and $Cd_{1-x}Mn_xTe$ [10]. For those compounds the crystal composition seemed not to influence the strength of the p–d hybridization. The change of the anion and the increase in the chemical bonding ionicity resulted in the simultaneous increase in the valence band component and decrease in the satellite (with respect to the main peak). Such a behaviour could be explained in terms of a CI cluster model as occurring due to the changes in the energy position of anion p-orbitals and in the p–d orbital overlap [9]. The results presented in this paper can hardly be interpreted this way. It seems that we have to consider interactions which were not included in the model based on the cluster built of an Mn ion and its nearest neighbours.

4. Summary

Photoemission spectroscopy was applied to determine the valence band density-of-states in $Mn_{0.44}Mg_{0.56}Te$ grown by MBE technique on a GaAs(001). The Mn 3*d* derived contribution to the electronic structure was revealed by resonant photoemission experiments. The results were compared with those obtained for other diluted magnetic semiconductors and for zb-MnTe. The changes of the valence band DOS caused by the presence of Mg atoms cannot be interpreted in terms of the CI cluster model successfully applied for other Mn-based DMS. We suppose that interactions ranging beyond the nearest neighbours have to be taken into consideration.

Further results concerning $Mn_{0.44}Mg_{0.56}Te$ crystals with different Mn contents could be a valuable contribution to the discussion about the dependence of *p–d* hybridization on the diluted magnetic semiconductor composition.

Acknowledgments

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References

[1] M.A. Haase, J. Qiu, J.M. DePuydt, H. Cheng, *Appl. Phys. Lett.* **59**, 1272 (1991).

[2] M.C. Phillips, M.W. Wang, J.F. Swenberg, J.O. McCaldin, T.C. McGill, *Appl. Phys. Lett.* **61**, 1962 (1992).

[3] A. Waag, H. Heinke, S. Scholl, C.R. Becker, G. Landwehr, *J. Cryst. Growth* **131**, 607 (1993).

[4] E. Janik, E. Dynowska, J. Bąk-Misiuk, T. Wojtowicz, G. Karczewski, J. Kossut, A. Stachow-Wójcik, A. Twardowski, W. Mac, K. Ando, *J. Cryst. Growth* **184/185**, 976 (1998).

[5] L.C. Davis, L.A. Feldkamp, *Phys. Rev. A* **17**, 2012 (1978); *Phys. Rev. B* **23**, 6239 (1981).

[6] R. Bruhn, B. Sonntag, H.W. Wolff, *Phys. Lett. A* **69**, 9 (1978).

[7] B.J. Kowalski, E. Guziewicz, B.A. Orłowski, E. Janik, G. Karczewski, T. Wojtowicz, J. Kossut, T. van Gemmeren, T. Buslaps, R.L. Johnson, *Thin Solid Films* **256**, 69 (1995).

[8] R.L. Johnson, J. Reichardt, *Nucl. Instrum. Methods Phys. Res.* **208**, 791 (1983).

[9] M. Taniguchi, M. Fujimori, M. Fujisawa, T. Mori, J. Souma, Y. Oka, *Solid State Commun.* **62**, 431 (1987).

[10] L. Ley, M. Taniguchi, J. Ghijsen, R.L. Johnson, A. Fujimori, *Phys. Rev. B* **35**, 2839 (1987).

[11] P.R. Bressler, H.-E. Gumlich, *J. Cryst. Growth* **138**, 1028 (1994).

[12] H. Sato, T. Mihara, M. Tamura, K. Mimura, N. Happo, M. Taniguchi, Y. Ueda, *Phys. Rev. B* **56**, 7222 (1997).