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Electronic structure of bulk ferromagnetic $Ge_{0.86}Mn_{0.14}Te$

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ABSTRACT

The electronic structure of polycrystalline $Ge_{0.86}Mn_{0.14}Te$—ferromagnetic semiconductor with $T_C = 110$ K, has been studied by means of resonant photoemission spectroscopy for photon energies close to the Mn 3p→3d excitation. The contribution of Mn 3d states to the electronic structure of the system was revealed and position of the Mn ions in the crystal, characteristic of GeTe-based diluted magnetic semiconductors was proved.

1. Introduction

The semiconducting solid solutions based on GeTe and containing Mn and Eu exhibit advantageous properties in view of applications in the expanding field of spintronics. The Curie temperature as high as 140 K for $Ge_{0.5}Mn_{0.5}Te$ (Fukuma et al., 2001), prospects of its increase due to co-doping with Eu (Dobrowolski et al., 2006) and existing technology of IV–VI-based devices make the idea of spintronic GeTe-based system quite realistic. It is also important that theoretical description of ferromagnetism in IV–VI semiconductors has been well developed. The ferromagnetic ordering in IV–VI-based diluted magnetic semiconductors (DMS) is governed by the Ruderman–Kittel–Yoshida–Kasuya interaction mediated by free holes related to native defects (Story et al., 1990; Cochrane et al., 1974). Change in the hole concentration by post-growth thermal treatment results in modification of the magnetic interaction in the crystal. In $Ge_{1-x}Mn_xTe$, the RKKY interaction competes with an antiferromagnetic superexchange mechanism and effects related to inhomogeneities in Mn distribution (Cochrane et al., 1974; Fukuma et al., 2003). Introduction of Eu into $Ge_{1-x}Mn_xTe$ makes the magnetic interaction scheme even more complicated (Dobrowolski et al., 2006). The mechanism of the T_C increase is still under debate, although hypotheses have been put forward, e.g. creation of Mn–Mn pairs was blocked by Eu ions or a mixed valence state of the system opened an additional channel of Mn–Mn interaction (Dobrowolski et al., 2006).

The valence band density of states distribution is one of the most important characteristics of semiconductors. For diluted magnetic semiconductors, the distribution of d and f states of magnetic ions against a background of the valence band plays the crucial role in description of magnetic, transport and optical properties of the system. Such information related to DMS based on GeTe was very limited and concerned only $Ge_{1-x}Mn_xTe$ (Senba et al., 2005). Our studies of bulk $Ge_{1-x-y}Mn_xEu_yTe$ (Kowalski et al., 2007) showed that the valence band states distribution differed markedly from that reported in the literature for $Ge_{1-x}Mn_xTe$ and from our results collected for epitaxial layers of $Ge_{1-x}Mn_xTe$ grown by MBE (Pietrzyk et al., 2007). Although the Mn 3d contribution to the valence band, derived from the resonance photoemission experiment, corresponds well to that reported for $Ge_{1-x}Mn_xTe$, the overall shape of the valence band is markedly different and suggests presence of some additional contribution. That inspired us to study the valence band of $Ge_{1-x}Mn_xTe$ grown by the same method as applied for $Ge_{1-x-y}Mn_xEu_yTe$. The main aim was assessment of the relation between Eu ions and irregular shape of the $Ge_{1-x-y}Mn_xEu_yTe$ valence band spectra.

The experimental method used in this study was resonant photoemission spectroscopy (RPES). In this technique, the radiation energy $h\nu$ is tuned to the intra-ion electron transition e.g. 3p–3d for transition metal atoms or 4d–4f for rare-earth atoms. Then, the regular photoemission process

$$3p^6 3d^n + h\nu = 3p^6 3d^{n-1} + e^- \text{ (for TM atoms)}$$

is accompanied by excitation of the ion

$$3p^6 3d^n + h\nu = [3p^5 3d^{n+1}]^*$$

The quantum interference between these two processes leads to autoionization

$$[3p^5 3d^{n+1}]^* \rightarrow 3p^6 3d^{n-1} + e^-$$

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and resonant photoemission described by the Fano formula (Fano, 1961)

$$I(h\nu) = I_0 \frac{(q+\varepsilon)^2}{\varepsilon^2+1} \quad (1)$$

where q is the symmetry parameter (Fano factor), ε the reduced energy variable which corresponds to the photon energy in photoemission experiments. A comparison of the photoemission spectra taken for photon energies corresponding to the minimum and maximum of the Fano profile reveals contribution of the open shell to the emission from the valence band. Therefore, RPES is used in order to determine the contribution of the 3d states of the transition metal atoms or the 4f states of rare-earth metal atoms to the electronic structure of the investigated crystal.

2. Experimental details

$Ge_{1-x}Mn_xTe$ ($x = 0.14$) polycrystal was grown by the Bridgman method in the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. $Ge_{1-x}Mn_xTe$ crystallized in a rhombohedrally distorted NaCl structure. The crystal structure was assessed by X-ray diffraction and no other phase was detected, within the sensitivity limits of the method. The chemical composition of the crystals was determined by means of energy-dispersive X-ray fluorescence analysis (Dobrowolski et al., 2006).

The clean crystal surfaces for the photoemission measurements were prepared *in situ* by scraping the sample with a diamond file under UHV conditions. The scraping was repeated, selected photoemission spectra were recorded and compared until further cleaning did not result in any change in the photoemission spectra. Then, we assumed that all surface-related impurities, oxides, etc. had been removed and all species contributing to the spectra were built into the bulk of the sample.

The magnetic properties of the samples were assessed by SQUID magnetometry, the morphology and elemental distribution were studied by scanning electron microscopy (SEM) with the use of a Hitachi SU-70 analytic microscope.

The electronic structure of $Ge_{0.86}Mn_{0.14}Te$ was studied by means of resonant photoemission spectroscopy. The spectra were measured for the photon energy range 40–60 eV (corresponding to Mn 3p→3d resonance). The resonant photoemission experiments were performed at the synchrotron radiation facility HASYLAB in Hamburg. Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the FLIPPER II plane grating vacuum monochromator designed for the photon energy range 15–200 eV. The total energy resolution was kept at 250 meV. The origin of the energy axis was set at the Fermi energy as measured for a reference metallic sample.

3. Results and discussion

Introduction of considerable amount of manganese into GeTe may lead to the formation of inhomogeneities and precipitates with modified chemical composition, especially close to grain boundaries in polycrystals. Such features can modify averaged magnetic properties of the system and photoemission spectra. Therefore, the morphology and elemental composition of the samples were tested by means of the scanning electron microscopy and energy-dispersed X-ray spectroscopy (EDS). Fig. 1 shows the morphology of the $Ge_{0.86}Mn_{0.14}Te$ sample in the vicinity of the grain boundary in the image formed by secondary electrons (Fig. 1a) as well as the image of the same part of the sample with increased atomic-number contrast (formed by back-scattered electrons) (Fig. 1b). Inhomogenities at the grain boundary and some individual tellurium precipitates were observed. However, the EDS analysis excluded, within the sensitivity limits of the method, marked increase of the manganese contents and appearance of considerable amount of manganese compounds other than $Ge_{1-x}Mn_xTe$, in those features. The elemental composition in other parts of the sample seems to be homogeneous.

The hysteresis appearing in the $M(H)$ function obtained by SQUID magnetometry (Fig. 2) shows that $Ge_{0.86}Mn_{0.14}Te$ polycrystal is ferromagnetic. No other magnetic system has been detected in the sample. The Curie temperature of this system is 110 K, markedly higher than expected from the T_C vs. x curve published by Chen et al. (2006).

A typical set of energy distribution curves of $Ge_{0.86}Mn_{0.14}Te$ for photon energies near to the energy of Mn 3p→3d transition is shown in Fig. 3a. The spectra cover the binding energy range from the valence band edge to 16 eV. The spectra were normalized to the photon flux, the origin of the binding energy scale was set at the Fermi energy measured for the reference metallic sample. The secondary electron background has been subtracted in accordance with the Shirley model. With an increase of the photon energy from 47.5 eV (antiresonant energy of the Fano-type resonance), the shoulder located at the binding energy of 3.8 eV (marked A in Fig. 3a) increases and reaches the maximum for $h\nu$ equal to 51 eV (resonance energy) and then moderately decreases with the increase of photon energy. The constant-initial-state (CIS) spectrum shown in Fig. 3b clearly confirms resonant behavior of this feature. The Fano resonance curve, corresponding to the experimental points, has the maximum at 51 eV and the anti-resonance minimum at 47.5 eV. Such a profile with the resonance

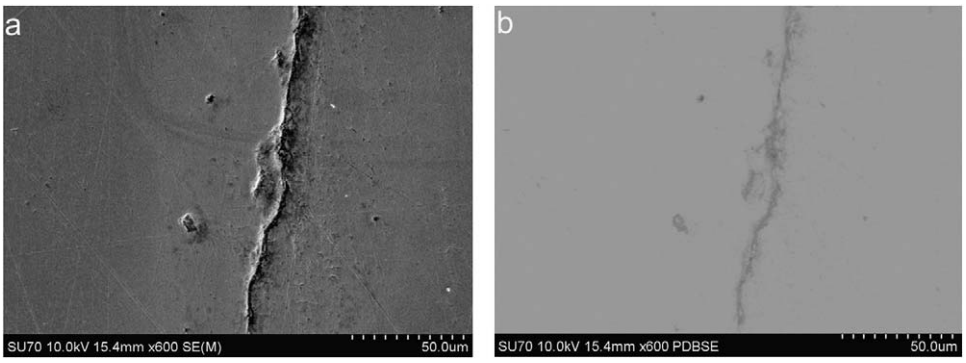

Fig. 1. The SEM images of the $Ge_{0.86}Mn_{0.14}Te$ sample taken with (a) secondary electrons and (b) back-scattered electrons.