Angle-resolved photoemission study and pseudopotential calculations of GeTe and Ge$_{1-x}$Mn$_x$Te band structure

B.J. Kowalski$^a$, M.A. Pietrzyk$^a$, W. Knoff$^b$, A. Łusakowski$^a$, J. Sadowski$^{b,a}$, J. Adell$^c$, T. Story$^a$

$^a$Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
$^b$MAX-lab, Lund University, Box 118, SE-22100 Lund, Sweden
$^c$Department of Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden

Abstract

The valence band structure along the $\Gamma$-T and T-W-L directions in the Brillouin zone of GeTe is studied by means of angle-resolved photoemission and compared with the results of \textit{ab initio} pseudopotential calculations. For Ge$_{1-x}$Mn$_x$Te surface alloy, changes in the valence band induced by presence of Mn atoms are revealed.

\textit{Key words:} germanium telluride, photoemission, band structure

1. INTRODUCTION

GeTe is a narrow-gap semiconductor which occurs in two crystalline structures: cubic (the rock salt structure) and rhombohedral (a distorted NaCl structure). It attracted recently a considerable interest due to magnetic phenomena discovered in GeTe-based diluted magnetic semiconductors (DMS) (in view of emerging spintronic applications). Ge$_{1-x}$Mn$_x$Te exhibited ferromagnetism with the Curie temperature which strongly depended on Mn concentration\cite{1} and could be as high as 190 K\cite{2}. Such properties of this material and their consistency with features expected for a good "spintronic" material have inspired extensive investigations of GeTe-related DMSs\cite{1, 2, 3, 4}.

The electronic band structure, density of states distribution and chemical bonding character of GeTe were theoretically investigated by several methods\cite{5, 6, 7, 8, 9, 10} for various forms of the crystal. The experimental results were limited only to X-ray photoelectron spectroscopy (XPS) data, showing the integrated density of states distribution\cite{10}. This paper reports an angle-resolved photoemission study of rhombohedral GeTe and Ge$_{1-x}$Mn$_x$Te surface alloy prepared by Mn deposition on the sample at the temperature of 200\textdegree C. The obtained results enable us to derive, for the first time, to our knowledge, experimental band structure diagram of GeTe.

$^a$E-mail address: kowab@ifpan.edu.pl
25.0 25.5 26.0 26.5
\( \alpha = 5.97163 \, \text{Å} \)

FWHM=325"

Intensity (arb. u.)

Figure 1: The X-ray rocking curve obtained for the epilayer of GeTe grown by MBE on BaF\(_2\)(111).

along the \( \Gamma - T \) direction in the Brillouin zone and compare it with the results of pseudopotential band structure calculations. We also compare the electronic states distribution along the T-W-L direction in GeTe and Ge\(_{1-x}\)Mn\(_x\)Te. The Mn 3d related contribution to the valence band has been detected.

2. EXPERIMENTAL DETAILS

The GeTe epilayers are grown by an MBE method on BaF\(_2\)(111) substrates. The substrate temperature is 400–450°C. The X-ray diffraction measurements, performed at room temperature, reveal monocrystalline (111)-oriented rhombohedral structure of the GeTe layers. The relatively small FWHM of the X-ray rocking curve, equal to 325 arcsec, (Fig. 1) proves good crystalline quality of the system.

The clean and ordered sample surface is prepared for photoemission experiments by cycles of \( \text{Ar}^+ \) ion sputtering and annealing under UHV conditions. This procedure results in the surface exhibiting hexagonal (1x1) LEED pattern. The angle-resolved photoemission experiments are performed with use of the photoelectron spectrometer at the beamline 41 in the MAXlab synchrotron radiation laboratory of Lund University (Sweden).

Manganese deposition is carried out in an MBE system, from a Knudsen cell. The GeTe substrate temperature is 200°C. The Mn flux is calibrated by measuring RHEED oscillations for GaMnAs(100) calibration samples [11]. During the growth of 1 ML of Mn on GeTe, Mn flux corresponds to the layer growth rate of 1 ML/min for metallic Mn.

We investigated a similar system by means of resonant photoemission spectroscopy [12]. A comparison of the spectra taken for Mn/GeTe and Ge\(_{0.5}\)Mn\(_{0.5}\)Te (doped during the MBE growth) showed close similarity of the shapes of Mn 3d contributions in these systems. That enabled us to claim that Mn atoms, delivered to the surface of GeTe, built into the GeTe matrix and a substitutional surface alloy Ge\(_{1-x}\)Mn\(_x\)Te was formed. The estimation based on a comparison of the
corresponding spectra of Mn/GeTe, Mn/Ge$_{1-x}$Mn$_x$Te and Ge$_{1-x}$Mn$_x$Te suggested that diffusion of 1 ML of Mn into the subsurface layer of GeTe resulted in formation of a surface alloy with an average Mn contents ($x$) of about 0.2.

3. RESULTS AND DISCUSSION

Fig. 2a shows the set of angle-resolved photoemission spectra taken for GeTe under normal emission conditions. The origin of binding energy axis is set at the Fermi energy, as measured for a reference metal sample. The secondary electron background has been subtracted by means of the Shirley method. The spectra acquired for the photon energy range from 17 to 50 eV enable us to map the valence band structure along the [111] direction from Γ to T. Fig. 2b shows the experimental band structure diagram derived from the spectra shown in Fig. 2a. The dots correspond to the spectral features found with the help of negative second derivatives. The lines show the GeTe band structure calculated using OpenMX package[13]. We use fully relativistic LDA pseudopotentials distributed with the program. The primitive cell of GeTe is characterized by three parameters: lattice constant, $a_0$, angle between neighbouring bonds, $\alpha$, and the position of Ge atom on the diagonal of the cell, $\tau$. In the calculations, we used their experimental values[14]: $a_0 = 5.987$ Å, $\alpha = 88.3^\circ$ and $\tau = 0.0248$. Best agreement between experimental E(k) diagram
and the results of calculation is obtained for the highest valence band. However, the position of the deeper bands at T deviates from the experimental results by about 0.5 eV. The dispersions of these bands also seem to be overestimated by the calculations.

We have performed additional calculations for several different sets of parameters $a_0$, $\alpha$, $\tau$. It turns out that the shape of the highest valence band depends mainly on $\alpha$. The agreement between calculations and experiment is much better for $\alpha < 90^\circ$ than for $\alpha > 90^\circ$. This is related to the fact that the GeTe/BaF$_2$ layer, with the thickness of 1 $\mu$m is relaxed and may be treated as a bulk crystal (if the layer was strained, due to lattice mismatch, the angle $\alpha$ should be greater than 90°).

For Ge$_{1-x}$Mn$_x$Te surface alloy, the band structure has been mapped along the T-W-L direction. By comparison of the data collected for GeTe and Ge$_{1-x}$Mn$_x$Te (Fig. 3), we are able to reveal the contribution of Mn 3d states to the valence band of the system. It appears mainly in the deeper part of the valence band (1.5-6 eV with respect to the valence band edge) with a maximum intensity at about 3.5 eV (Fig. 4). No additional density of states manifests itself at the Fermi energy. This proves that most of deposited manganese atoms have been bound in the surface region of the GeTe layer and amount of metallic manganese at the surface is negligible.
Figure 4: The difference spectrum obtained by the subtraction of the GeTe spectrum corresponding to the T point in the Brillouin zone from the corresponding curve acquired for Ge$_{1-x}$Mn$_x$Te.

The revealed distribution of the manganese related states in the valence band of Ge$_{1-x}$Mn$_x$Te is consistent with that recently calculated with use of the density-functional theory[15].

4. SUMMARY

The valence band structure along the Γ-L and T-W-L directions in the Brillouin zone has been determined for GeTe by means of angle-resolved photoelectron spectroscopy. We compare the experimental results with the band structure calculated by means of the fully relativistic LDA method. The calculations are carried out for several sets of crystallographic parameters, corresponding to different distortions of the rock-salt lattice. The best correspondence between the experimental and theoretical results is achieved for the set describing a relaxed GeTe layer.

A comparison of the photoemission spectra taken for GeTe and Ge$_{1-x}$Mn$_x$Te surface alloy indicates that manganese atoms dope the surface layer of GeTe and that Mn gives a contribution to the valence band distributed in the binding energy range of 1.5-6 eV.

5. ACKNOWLEDGEMENTS

The authors acknowledge support by MSHE (Poland) grants N202 101 31/0749 (2006-2009), 0992/T02/2007/32 (2007-2010) and as a part of common research of the scientific network "New materials - production and structure investigation" as well as by the European Community - Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science") via MAXlab, Lund University.
References