Cr $3d$ SURFACE AND BULK STATES IN $Sn_{1-x}Cr_xTe$/Cr CRYSTALS*

E. Guziewicz, K. Szamota-Sadowska, B.J. Kowalski, E. Grodzicka, T. Story, B.A. Orlowski

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland

AND R.L. Johnson

Universität Hamburg, II Institut für Experimentalphysik
Luruper Chaussee 149, 22761 Hamburg, Germany

We report a new approach to investigate metal–semiconductor interface formation. Photoemission spectroscopy was applied in order to investigate the clean surface of a $Sn_{0.97}Cr_{0.03}Te$ crystal and to observe its changes under sequential deposition of small amounts of Cr atoms. In order to analyse the Cr $3d$ contribution to the valence band, the Fano-type resonance tuned to the Cr $3p$–$3d$ transition was used. The experiment was designed to follow the $Sn_{0.97}Cr_{0.03}Te$/Cr interface formation process. At the clean $Sn_{0.97}Cr_{0.03}Te$ surface, the Cr $3d$ states contribution to the valence band was found to be positioned 0.8 eV below the Fermi level. After the Cr deposition processes the contribution shifted to a higher binding energy and another contribution 5.8 eV below the Fermi level was also observed.

PACS numbers: 79.60.–i, 68.35.Fx

1. Introduction

The presence of localised magnetic ions in diluted magnetic semiconductors (DMS) leads to such important magnetic and optical effects as spin-glass-like phase at low temperatures or highly efficient electroluminescence, which is important in display device applications. The magnetic properties of transition metal ions are determined by electrons partially occupying the $3d$ shell. The position of energy levels corresponding to $3d$ orbitals of TM (TM — transition metal) with respect to the band structure of the parent semiconductor affects the sp–d and d–d exchange interaction and in this way determines the magnetooptical properties of DMS.

The presence of Cr in the $Sn_{0.97}Cr_{0.03}Te$ crystal introduces two energy levels corresponding to the majority $e_d^{+\sigma}$ (occupied) and to the minority $e_d^{-\sigma}$ (unoccupied) states of the $3d$ orbital. In a real semiconductor these levels will be further

---

split by the crystal field and broadened into narrow bands by hybridization with valence band orbitals.

Photoemission spectroscopy is a powerful tool for band structure investigations. Resonant photoemission spectroscopy tuned to TM $3p$–$3d$ core resonances allows the study of the contribution of the TM ions $3d$ electrons to the valence bands of DMS [1–3].

In this paper we present the application of resonant photoemission spectroscopy to the investigation of the Schottky barrier formation. By this method we followed the changes in the density of states of the $Sn_{0.97}Cr_{0.03}Te$ crystal before and after sequential deposition of small amounts of Cr atoms. Differences in $3d$ electron contributions to the valence band of the $Sn_{0.97}Cr_{0.03}Te$ both in the bulk and on the surface were also analysed.

2. Experimental conditions

The reported photoemission experiment was carried out in a photoemission spectrometer attached to the beam line Flipper II of the Storage Ring DORIS II in HASYLAB at DESY in Hamburg, Germany. Synchrotron radiation was used in the photon energy range of 40–80 eV. The energy resolution was 0.2 eV [4].

The $Sn_{0.97}Cr_{0.03}Te$ crystal was grown at the Institute of Physics, Polish Academy of Sciences (Warsaw, Poland) by a modified Bridgman method. The clean surface was obtained by cleavage of the sample under UHV conditions ($p = 3 \times 10^{-10}$ Tr). The photoemission spectra were measured *in situ*.

3. Results and discussion

The experiment was designed to follow the interface formation process of the $Sn_{0.97}Cr_{0.03}Te/Cr$ interface. A resonant photoemission technique was used to reveal the Cr $3d$ contribution to the electronic structure of the system under investigation. Energy distribution curves (EDC's) were acquired at photon energies corresponding to the intra-atomic Cr $3p$–$3d$ transition. The Fano-type resonance leading to the increase in electron photoemission from the Cr $3d$ states helped us to analyse the $3d$ contribution to the valence band of the crystal.

Figure 1 presents a set of EDC's acquired for the freshly cleaved surface of the $Sn_{0.97}Cr_{0.03}Te$ crystal for photon energies ranging from 43 to 49 eV. The EDC for the photon energy far from the Fano-type resonance shows an extended valence band located in the energy region from 0 to 14 eV below the Fermi level. When the photon energy is tuned to a Cr $3p$–$3d$ energy of 49 eV, one can observe the well visible changes in EDC's. Comparing EDC taken for 49 eV with other EDC's presented in Fig. 1, one can notice a contribution of the Cr $3d$ state at the edge of the valence band with a maximum 0.8 eV below the Fermi level.

The constant initial states (CIS) spectra taken for the initial state 6.25 eV below the Fermi level, after the first, second and third Cr evaporation processes, showed the same resonant and antiresonant energies as the clean $Sn_{0.97}Cr_{0.03}Te$ crystal. EDC's for photon energies of 44, 47 and 49 eV were taken after each step of the Cr evaporation process. In Fig. 2a, the EDC's acquired for the photon energy of 49 eV are shown for each step of the Cr deposition. We chose the energy of 49 eV, as the resonant energy of chromium, so one can assume that the contributions of Cr
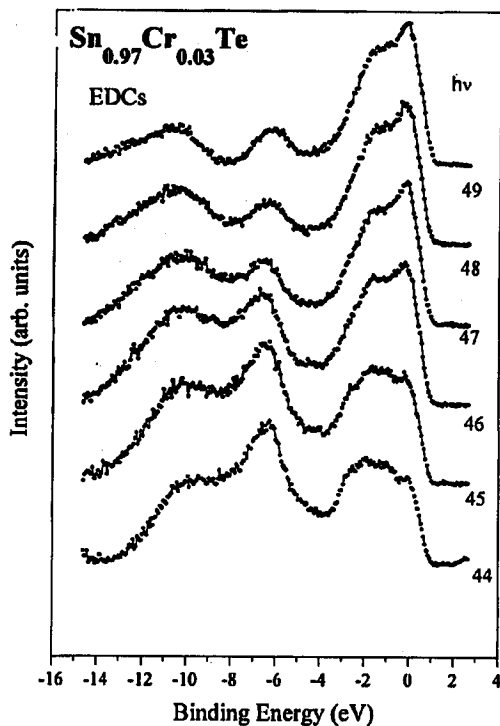
Fig. 1.   The set of energy distribution curves taken for clean $Sn_{0.97}Cr_{0.03}Te$ surface.

$3d$ states will be very visible. In Fig. 2b the EDC taken for the clean $Sn_{0.97}Cr_{0.03}Te$ surface was subtracted from the EDC's taken after the first, second and third Cr deposition in order to clearly show the contribution from evaporated chromium.

In Fig. 2a and 2b we can observe, after each Cr evaporation process, the considerable increase in photoemission at an energy near 0.8 eV — an energy characteristic of Cr $3d$ contribution to the valence band of the crystal. This EDC structure shifts about 0.5 eV towards larger binding energies: from 0.8 eV for $Sn_{0.97}Cr_{0.03}Te$ crystal to 1.3 eV below the Fermi level for $Sn_{0.97}Cr_{0.03}Te/Cr$ after the third Cr evaporation process. Such a shift towards a bigger binding energy can be regarded as the manifestation of the band bending due to the metal–semiconductor interface formation. Apart from a strong enhancement of the A photoemission maximum, for EDC corresponding to the second and third Cr deposition, one can notice the B structure at an energy 5.8 eV below the Fermi level. Taking into account the Cr $3d$ splitting in the crystal field, the A structure is probably caused by photoemission from $3d_e$ electronic sublevel. The B structure may be regarded as caused by photoemission from $3d_{t_2}$ electronic sublevel. The occurrence of the density of states observed at the B maximum in EDC spectra (Fig. 2a) can be used as an argument for the creation of a $Sn_{1-x}Cr_xTe$ ternary compound with a higher x value. The origin of the wide structure with the maximum about 11 eV below the Fermi level seems to be related to the Auger effect. This Auger effect can
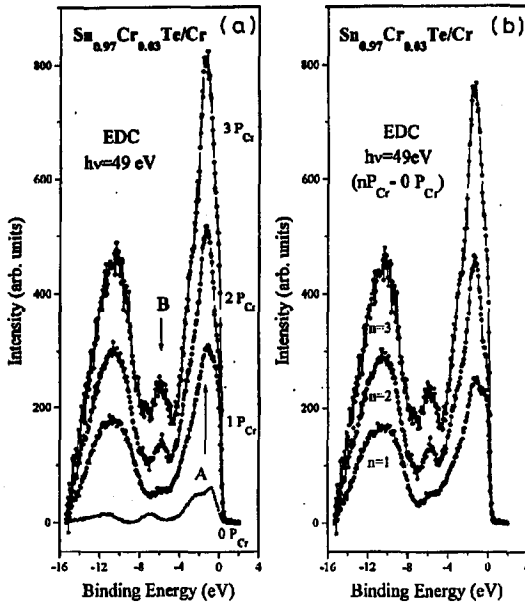
Fig. 2. (a) The set of energy distribution curves acquired at photon energy equal to 49 eV for clean surface of $Sn_{0.97}Cr_{0.03}Te$ (0 P_{Cr}) and after first (1 P_{Cr}), second (2 P_{Cr}) and third (3 P_{Cr}) chromium deposition. (b) The set of difference of EDC's taken at 49 eV for $Sn_{0.97}Cr_{0.03}Te/Cr$ crystal after the first, second and third Cr deposition and EDC taken at the same energy for clean surface of $Sn_{0.97}Cr_{0.03}Te$ crystal.
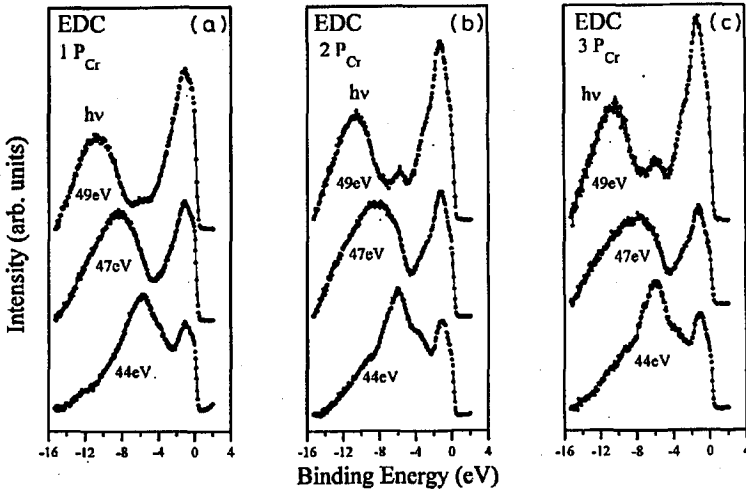

Fig. 3. The set of EDC's in $Sn_{0.97}Cr_{0.03}Te/Cr$ obtained after: (a) the first, (b) the second, (c) the third chromium deposition.

be easily observed in Fig. 3a, 3b and 3c, which show the photoemission for 44, 47 and 49 eV for every stage of Cr evaporation. In these figures we can notice a considerable increase in photoemission near the valence band edge and a shift of the second distinct maxima towards higher binding energies. This shift is equal to 2 eV between EDC spectra taken for 47 and 49 eV, and to about 3 eV between EDC spectra acquired for 44 and 47 eV. This fact provides evidence for the Auger origin of this effect.

4. Summary

The metal–semiconductor $Sn_{0.97}Cr_{0.03}Te/Cr$ interface formation was investigated by means of resonant photoemission spectroscopy. The resonant and antiresonant energies were determined to be 49 and 44 eV. A set of energy distribution curves was measured for a clean surface of the $Sn_{0.97}Cr_{0.03}Te$ crystal, and then after each step of Cr deposition. In the case of a clean $Sn_{0.97}Cr_{0.03}Te$ surface, Cr $3d$ states give a contribution at 0.8 eV below the Fermi level. After the second and third Cr deposition, the contribution of Cr $3d$ states increases and shifts towards higher binding energies due to the Schottky barrier formation. Another contribution with a smaller intensity was also observed at an energy 5.8 eV below the Fermi level and it is attributed to $3d_t$ electrons.

References

[1] R.L. Lad, V.E. Henrich, *Phys. Rev. B* **39**, 13478 (1988).

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

[3] R. Denecke, L. Ley, J. Fraxedas, *Phys. Rev. B* **47**, 13197 (1993-II).

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