$Cd_{1-x}Fe_xSe$/Fe INTERFACE FORMATION OBSERVED BY MEANS OF PHOTOEMISSION SPECTROSCOPY*

E. Guziewicz, B.A. Orlowski, B.J. Kowalski

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

N. Barrett, D. Martinotti, C. Guillot

Laboratoire pour l'Utilisation du Rayonnement Electromagnetic
Bat. 209 D, Centre Universitaire Paris-Sud, 91405 Orsay Cedex, France
and DRECAM-SRSIM, CE Saclay 91191 Gif sur Yvette, France

J.-P. Lacharme and C.A. Sebenne

Laboratoire de Physique des Solides, ERS 113 au CNRS, Case 79
Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

We present a new outlook at the study of metal–semiconductor interface formation. A resonant photoemission spectroscopy tuned to the Fe $3p$–$3d$ transition (56 eV) was used to investigate the changes after sequential deposition of Fe atoms on freshly cleaved $Cd_{0.86}Fe_{0.14}Se$ crystal surface. In the first stages (0.6–4 ML) of Fe deposition the contribution of Fe $3d$ electrons to the valence band grows up markedly indicating the increase in Fe content in the $Cd_{0.86}Fe_{0.14}Se$ crystal surface region. When the amount of Fe exceed 40 ML the resonant photoemission spectra became similar to the Fe metal with some contribution of the ternary crystal substrate.

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1. Introduction

The dominant sources of interesting magneto-optical properties of diluted magnetic semiconductors (DMS) are: (1) the random distribution of transition metal (TM) atoms substituting for cation sites, and (2) the exchange interaction of the TM $3d$ electronic states with the electronic states of the parent semiconductor. A very important effect is the hybridization between the TM $3d$ states and the parent semiconductor sp valence band states [1, 2]. Resonant photoemission spectroscopy with the use of synchrotron radiation is a powerful tool for distinguishing the partial contribution of TM $3d$ electrons to the valence band [3].

The Fano-like resonance is the result of interference between the direct photoemission process of TM $3d$ electrons and the discrete TM $3p$–$3d$ transition followed by a super-Coster–Kronig decay. In the resonant photoemission process the photon energy is tuned to the absorption edge region of the TM $3p$–$3d$ transition in order to excite TM ions selectively and locally.

We used Fano-like resonance to follow the changes in the Fe $3d$ electron contributions to the valence band of the $Cd_{0.86}Fe_{0.14}Se$ crystal during sequential deposition of a small number of Fe atoms. We were able to distinguish the differences in the energy distribution curve (EDC) spectra caused by both bulk and surface Fe derived states and to investigate the process of $Cd_{0.86}Fe_{0.14}Se/Fe$ metal–semiconductor interface formation.

2. Experimental conditions and results

The experiment was carried out in a spectrometer attached to the line SA71 (TGM 2.5 m) of the storage ring SUPER-ACO in LURE, Orsay, France. The synchrotron radiation was used in the photon energy range of 20–130 eV with the resolution kept between 150 and 300 meV. The $Cd_{0.86}Fe_{0.14}Se$ samples were grown by the modified Bridgman method at the Institute of Physics, Polish Academy of Sciences, Warsaw, Poland. The clean surface of the sample was obtained by cleavage using a knife-anvil technique under UHV conditions ($p = 1 \times 10^{-10}$ torr). The Fe flux was obtained from a Joule-heated pure Fe wire. The amount of Fe atoms deposited on the surface was measured by means of the quartz resonator.

Energy distribution curves (EDCs) were acquired at the photon energy range including the intra-atomic Fe $3p$–$3d$ transition (56 eV). Figure 1 presents the set of EDCs taken for different amounts (0–4 ML) of Fe atoms deposited on the $Cd_{0.86}Fe_{0.14}Se$ crystal. The EDCs were obtained for Fe $3p$–$3d$ resonant energy equal to 56 eV. In the EDC acquired for the clean crystal surface one can observe the valence band of ternary compound extending to the 6 eV below the valence band edge. At 0.5 eV a small maximum is visible. This structure, as well as that observed at about 2.25 and 3.8 eV below the valence band edge, are believed to be fingerprints of the Fe $3d$ electrons [4]. The maximum at 0.5 eV arises due to the contribution of the Fe $3d$ spin down electron whereas the maxima at 2.25 and 3.8 eV correspond to the contribution of five Fe $3d$ spin up electrons [4]. The positions of these maxima are consistent with those obtained by Denecke et al. [5] for $Cd_{1-x}Fe_xSe$ crystals. Even a deposition of small amounts of iron atoms changes considerably the spectra shown in Fig. 1. At every point of energy the intensity of EDC consists of the photoemission from the bulk $Cd_{1-x}Fe_xSe$ crystal and from the Fe atoms deposited on the crystal surface. However, the uniform increase of $3d_{e\uparrow}$, $3d_{t\uparrow}$ and $3d_{e\downarrow}$ peaks, connected with Fe bulk states, may be treated as a sign of the creation of the $Cd_{1-x}Fe_xSe$ ternary crystal with a higher x value. Such an interpretation is supported by the previous investigations of the $Cd_{1-x}Fe_xSe/Fe$ Schottky barrier formation [6]. The $3d_{e\uparrow}$, $3d_{t\uparrow}$ and $3d_{e\downarrow}$ rise proportionally only for 0.6 ML of the iron deposition. For the next steps of deposition the photoemission at 0.5 eV below the valence band edge rises more clearly, because it is enriched by photoemission from Fe islands. These islands start to grow at the surface of the crystal. For the next steps of Fe deposition we can observe at the edge of EDC
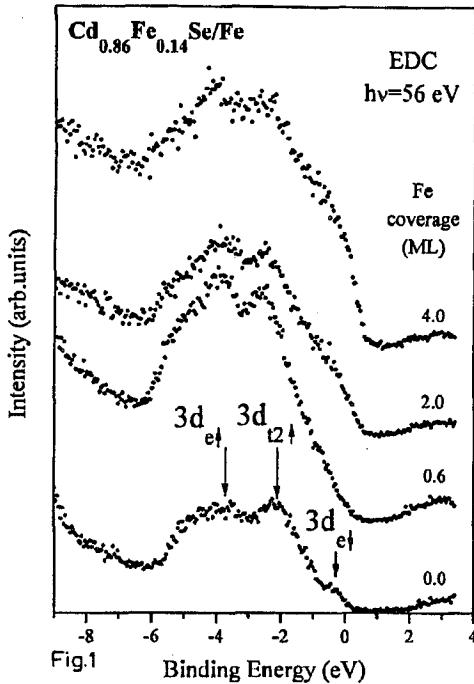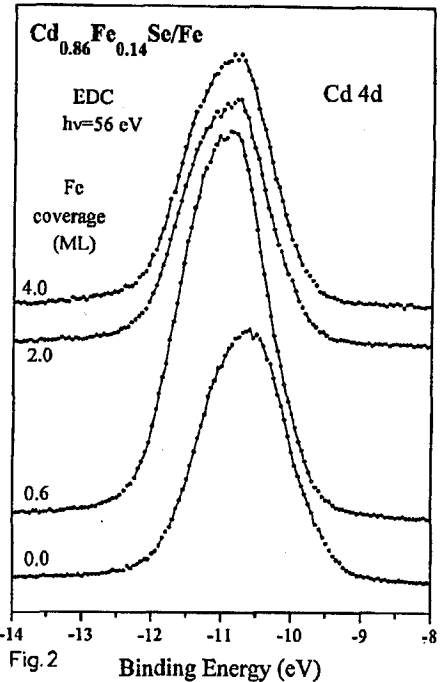
Fig. 1.   The set of EDCs taken for different amounts (0–4 ML) of deposited Fe atoms on Cd$_{0.86}$Fe$_{0.14}$Se crystal obtained for resonant energy 56 eV.

Fig. 2.   The set of EDCs containing Cd $4d$ band measured for the increasing amount of deposited Fe atoms (0–4 ML). The shift of the maximum by 0.3 eV is the evidence of Schottky barrier formation.

the contribution of Fe atoms covering the crystal surface. For the deposition of 40 ML of Fe, the edge of EDC corresponds well to the Fe crystal spectra [7].

Figure 2 presents the set of EDCs spectra containing Cd $4d$ band taken for Fe resonant energy equal to 56 eV. The spectra were acquired from 0 to 4 ML of deposited Fe atoms. The Cd $4d$ level obtained for the clean Cd$_{0.86}$Fe$_{0.14}$Se crystal surface does not show the spin–orbit splitting typically observed in Cd metal and CdSe crystal compound [8]. The reason seems to be in the presence of the local structure created by the Fe atoms located at the site of the Cd atom.

After the first step of Fe deposition the position of Cd $4d$ maximum increases by about 0.3 eV. This effect can be explained as a result of band bending, which accompanies a Schottky barrier formation process. After the next steps of iron deposition the binding energy of Cd $4d$ level is still located at -10.8 eV, though its shape changes a little as a consequence of the change of the Cd next nearest neighbours from Cd to Fe.

3. Summary

A resonant photoemission technique was applied for the investigation of the Cd$_{0.86}$Fe$_{0.14}$Se/Fe interface formation. In the first stages of Fe deposition the con-

tribution of Fe $3d$ electrons to the valence band well corresponds to the increase in x in the ternary crystal. When the amount of Fe exceeds 40 ML, the photoemission spectra become similar to those of the Fe metal, with a small contribution of the ternary crystal substrate. A Schottky barrier formation manifests itself in 0.3 eV shift of Cd $4d$ level towards a higher binding energy.

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