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**Photoemission Study of Clean Surface of Semiconductors
with Introduced Metal Atoms**

The electronic structure of the surface of semiconductors can be influenced by the atoms adsorbed on the surface as well as by the introduction of these atoms into the bulk of the crystal as an impurity or ternary alloy component. The two photoemission spectroscopies will be presented: ultraviolet photoemission (UPS) and yield photoemission spectroscopy (YPS) for the case when the additional atoms are introduced into the volume of the crystal as a third component and for the case when additional atoms will be deposited on the surface of the crystal. The case of introduction of the atoms into the volume of CdF_2 crystal will be presented for ternary crystal $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ using the ultraviolet photoemission spectroscopy (UPS) results. The case of p-type CdTe (110) surface covered by oxygen and by In atoms will be presented as an example how the atoms deposited on the surface influence on the yield photoemission spectra.

INTRODUCTION

The interest of investigation of the electronic structure of the surface and the region near to the surface is strongly stimulated by the tremendous possibilities to apply the electronic properties of this region using the small amount of semiconductor material and to create the microelectronic devices. The main electronic properties of microelectronic devices are strongly dependent on the electronic properties of the crystal surface and the region nearest to the surface. For some properties the surface region is concern to the atoms positioned on the surface (e.g. if one considers adsorption of atoms on dangling bonds on the reconstructed surface) while for the another cases it can be concern to the distance equal to the several distances of atomic nearest neighbours (e.g. crystalline lattice reconstruction on the freshly cleaved surface of the crystal in the UHV conditions). In the case of the free electrons distribution in the semiconductor surface region it can be comparable to the surface band bending region or to the Debay length (e.g. several hundreds of Angstroms).

To investigate electronic structure properties of the surface and surface region the electronic transitions in this region can be investigated using the highly absorbed vacuum ultraviolet radiation or low energy electron radiation. The absorption coefficient of vacuum ultraviolet radiation in solids is about 10^6 cm^{-1} and this radiation penetrates into the solid on the distance of about hundred of Angstroms. Some of the electrons excited in the crystal over the vacuum level can escape from the crystal. The escape depth of these electrons (the distance on which the number of escaping electrons decreases e-times) can be on about one order lower than the penetration depth of the vacuum ultraviolet radiation [1,2]. The value of escape depth of the electrons depends on kinetic energy of the electrons and changes from value of several Angstroms, for kinetic energy equal 80 eV, up to the value of several hundreds of Angstroms for kinetic energies out of the minimum [1,2]. The energy and the momentum of the escaping electrons can be analyzed and the tremendous amount of the informations on the valence band electronic structure of the surface and the surface region can be obtained. Modern equipment of the photoemission electron spectroscopy (PES) experiment with the synchrotron radiation, with electron lasers and with precise angle resolved analyzers joined in computerized system, features the following mentioned possibilities to investigate the electronic structure of the valence band of the surface and the surface region [1,2,3]: (1) to

distinguish the contribution of the surface and bulk states to the obtained energy distribution curve (EDC) by measuring the change of the EDC when varying the exciting energy $h\nu$ around the minimum of the escape depth ($E = 80$ eV) and outside of this region. (2) To discriminate in the valence band the contribution of the d-electrons from that of the s-p electrons due to a different change of the photoemission cross section of the d and s-p electrons with a change of $h\nu$. (3) to recognize the localized and delocalized electrons contribution to the density of states in the valence band and to determine $E(k)$ - energy-momentum dependence for these electrons by measurement of the angle resolved EDCs. (4) To obtain information on the initial and final states distribution using the constant initial states (CIS) and/or constant final states (CFS) techniques. (5) To recognize the contribution of the valence electrons of the particular atom to the valence band of the many component crystal using the EDC measurement for $h\nu$ radiation in the region of the resonant photoemission for this atom [3].

The purpose of the paper is to present how the atoms introduced into the volume of the crystal or on the surface of the crystal contribute to the photoelectron spectra. The case of introduction of the atoms into the volume of the crystal will be presented for CdF_2 crystal with introduced atoms of Pb on the seat of Cd atoms. The case of atoms deposited on the crystal surface will be presented for clean surface of CdTe crystals with adsorbed oxygen and deposited atoms of In.

EXPERIMENTAL CONDITIONS

The study were performed on two kind of experimental systems: (1) The commercial spectrometer ADES-400 produced by Vacuum Generator Scientific Ltd and (2) the home made in the laboratory of the Institute of Physics Polish Academy of sciences the UHV chamber joined with vacuum ultraviolet monochromator MV-8 [4]. The spectrometer ADES-400 is equipped with the UPS, XPS and LEED facilities working in UHV ($p=10^{-10}$ Torr) [5]. The energy resolution of the analyzer was kept at 0.1 eV for UPS experiments and 1 eV in XPS measurement. The electron energy analyzer can measure the electrons photoemitted for different angles relatively to the perpendicular to the crystal surface. For UPS measurement, a de-excited resonance discharge lamp source was used with two stages differential pumping system. The He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) excitation photon beams can be separated in a grazing incidence ultraviolet monochromator V.G.UVM 100 connected in series with a UV lamp. The angle of light incidence was 45° measured with respect to the surface normal. The data acquisition and

storing have been performed by a V.G. Data System 4025 on line computer based on DECLSJ 11/2 processor. The samples were clipped to the sample holder of the standard UM 20 manipulator. The samples surface was cleaned in the spectrometer chamber by argon ion bombardment and annealing. An Au sample was used to calibrate the energy scale and to determine Fermi level position.

The second system permitted to measure the Yield Photoemission Spectra for clean freshly cleaved in situ surfaces and for this surfaces covered by adsorbed oxygen and deposited in metal atoms. The clean surface of CdTe p-type was obtained by cleavage in UHV chamber ($p = 10^{-9}$ Torr) to reveal smooth mirror like (110) surface $4 \times 5 \text{ mm}^2$ and all measurement were performed in situ. As a monochromatic light source the vacuum monochromator MV-8 ($h\nu$ up to 12 eV) was used. The light was introduced to the UHV chamber by LiF window [4]. As a light detector the sodium salicylate, deposited on a glass plate, with photomultiplier were used. The photocurrent was measured by an ECCO electrometer (sensitivity 10^{-15} A).

ATOMS INTRODUCED INTO THE VOLUME

Let's consider the change of electron binding energy of isolated ion

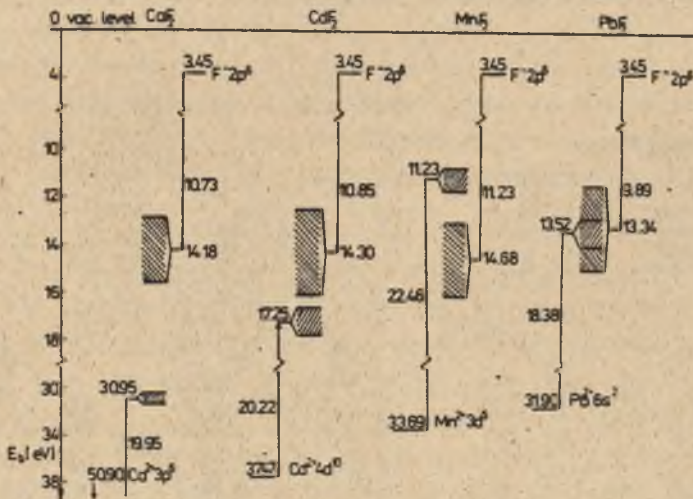


Fig.1 The binding energy of the valence band electrons and the nearest to it core levels according to the Madelung energy calculations for CaF_2 , CdF_2 , MnF_2 and PbF_2 [5]. Zero of the energy scale is in the vacuum level.

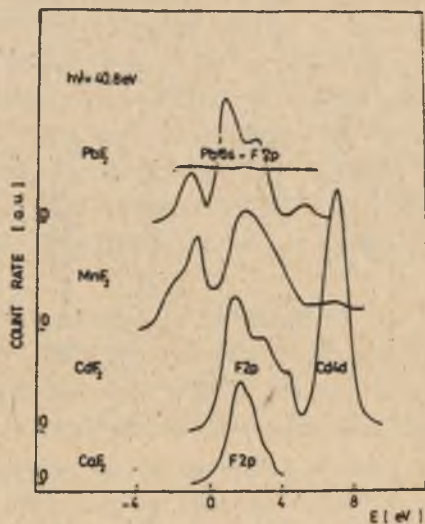


Fig.2 The set of EDC's of the valence band region and the nearest core levels of CaF_2 , CdF_2 , MnF_2 and PbF_2 crystals [5]. Zero of the energy scale is shifted on about 12 eV in comparison to the scale in Fig.1 and correspond to the valence band edge of CaF_2 .

when it is introduced into the crystal. As an electron binding energy we will take the distance of the particular level from the vacuum level. In Fig.1 the binding energies of the valence band electrons of the isolated ions are presented for CaF_2 , CdF_2 , MnF_2 and PbF_2 compounds. The considered crystals are highly ionic with the cations charge +2 and the anion charge -1. The biggest binding energies presented in Fig.1 correspond to the electrons with the lowest binding energy in the particular +2 cations: 50.9 eV, 37.47 eV, 33.69 eV and 31.9 eV - the third binding energies of the Ca, Cd, Mn and Pb atoms respectively [6]. The lowest binding energy (3.45 eV), presented on Fig.1, correspond to the lowest binding energy of the electrons on F^- ion. This all ions located in to the crystal lattice shift their binding energies on the value equal to the potential created by the surrounding of it particular ion all of the ions in the crystal (the Madelung energy [6]). Those shifts determine the new binding energies of the electrons in the created crystals. For CaF_2 the valence band will be build of $\text{F}^- 2p^6$ electrons [6] with binding energy of about 14 eV, and the nearest to the valence band core level will be located far down with the binding energy equal about 30.95 eV. For the case of CdF_2 the valence band of the crystal will be build as well of $\text{F}^- 2p^6$ [6,7] electrons but the

nearest core level will be located close to the valence band edge. In a case of MnF_2 [8,9] the inverted situation appears and the $Mn^{+2}3d^5$ electrons will mainly create the valence band edge, while the $F^{-2}2p^6$ electrons will contribute to the lowest part of the valence band. For the case of PbF_2 [6,10,11,12] the $Pb^{2+}6s^2$ electrons will be a resonant to the $F^{-2}2p^6$ electrons. All of the expected electron levels positions (they correspond to the center of gravity of the created of them bands in the crystals) are very well confirmed by the experimental data presented in Fig.2 [5].

As the binding energy scale in Fig.2 is shifted on about 12eV in comparison to the vacuum level position presented in Fig.1, so the valence band edge of CaF_2 and CdF_2 determine the zero of the energy scale. For CdF_2 crystal the Cd 4d electrons are located below the valence band build of $F^{-2}2p^6$ electrons while for the MnF_2 crystal it is above the $F^{-2}2p^6$ electrons band. The resonant $Pb^{2+}6s^2$ electrons interact with the $F^{-2}2p^6$ electrons giving two additional density of states located in the upper and the lower part of the valence band.

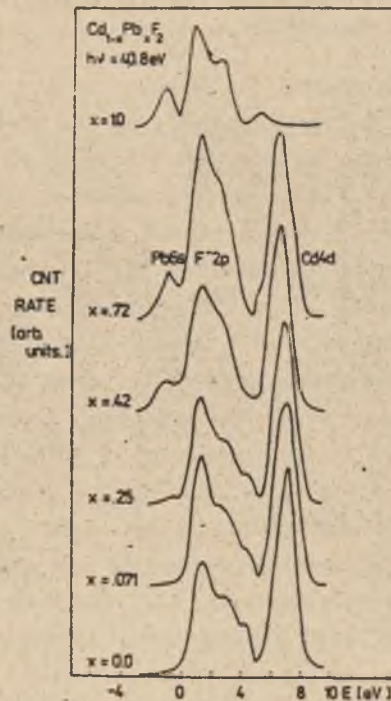


Fig.3 The set of energy distribution curves of the valence band of the ternary crystal $Cd_{1-x}Pb_xF_2$ with different composition x [5].

The introduction of ions like Ca^{+2} [5], Mn^{+2} [5,8] or Pb^{+2} [5,10,11,12] into the seat of Cd^{2+} ions in CdF_2 crystal leads to the remarkable changes of the density of states distribution in the ternary alloys. The UPS spectra of the valence band region of $\text{Cd}_{1-x}\text{Pb}_x\text{F}_2$ crystals are presented in Fig.3 for different atomic compositions x of the crystals. In the first approximation the measured density of states distribution in the valence band of the ternary crystals can be approximated as a sum of the density of states of its compounds taken with their contribution x and $1-x$ respectively. The interaction between the electrons of the compounds and introduced crystalline disorder leads to the deviation from this first approximation.

ATOMS DEPOSITED ON THE SURFACE

The freshly cleaved in UHV CdTe crystal (zinc blund structure) surface (110) reconstruct' by this way that the Te atoms move up over the previous surface position and the direction of Cd-Te bonding in the top layer changes on the angle of 30° relatively to the direction in the crystal before cleavage [13]. The adsorption of the new atoms on the reconstructed surface leads to the re-reconstruction of the atoms on the surface and to the creation of the new, surface like, ternary alloy $\text{Cd} +$

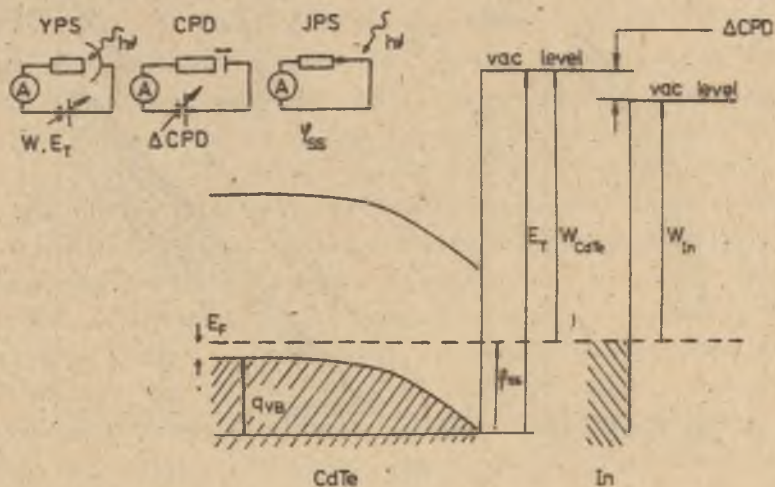


Fig.4. Diagram of the energy levels near the semiconductor and metal surface with insert of three schemes of experiment: YPS, CPD and IPS. W -work function, E_t - photoemission threshold, q_{vb} -band bending energy, ϕ_{ss} and E_T the Fermi level position at the surface and bulk respectively.

Te + M (M-deposited atom). It leads to the rearrangement of the electrons at the surface and to the creation of the new electronic structure in the surface region. New distribution of the electrons in the surface region can lead to the change of the potential of the surface and to the appearance of new band bending conditions in the surface region. The reaction of the deposited atoms with the surface can lead to the electron transfer from the deposited atoms to the crystal surface region and to create the dipol layer in the interface region. In this case the affinity of the electrons in the crystal can decrease and it is causing the shift of the spectral dependence of the photoemission yield in the direction toward to the lower $h\nu$ energies. In Fig.4 the diagram of the energy levels on the surface and at the band bending region of CdTe (p) crystal clean surface after oxygen adsorption and then the In metal deposition is presented. At the left top corner in Fig.4 the schemes of three experiments are presented: YPS - Yield Photoemission Spectroscopy, CPD - Contact Potential Difference and IPS - Internal Photoemission Spectroscopy. The set of these experiments gave the possibility to determine all of the parameters presented in diagram of the energy levels

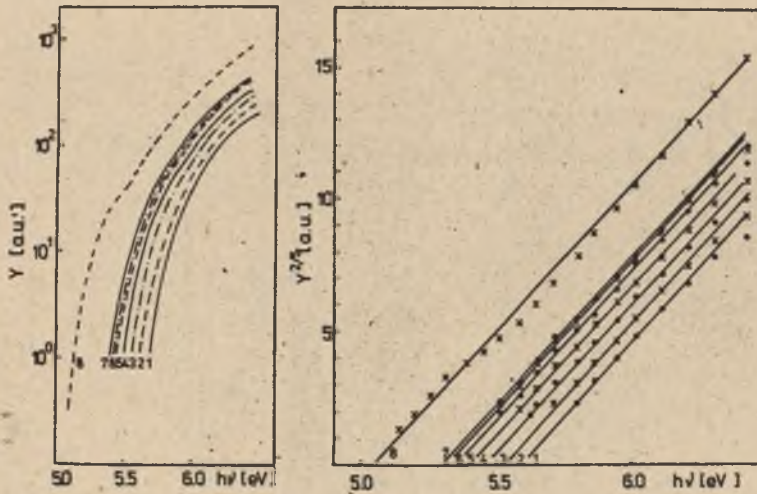


Fig.5. Spectral dependence of the photoemission yield (a)-log. scale; (b) - $[\text{h}\nu - E_T(t)]^{5/2}$ scale) for various exposure time of the CdTe (p) (110) surface to 10^{-4} Torr: (1), 30 min; (2), 60 min; (3), 90 min; (4), 135 min; (5), 170 min; (6), 215 min; (7), 265 min; (8), 1400 min [14].

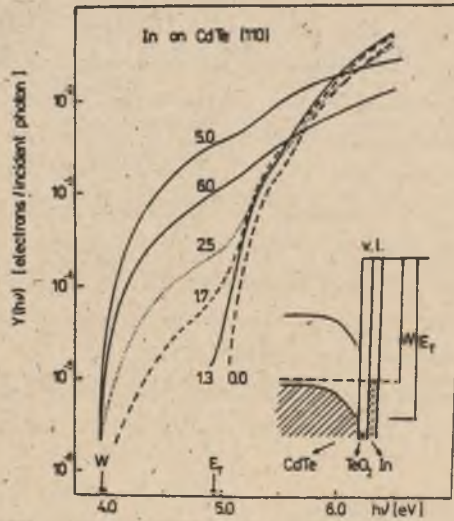


Fig.6 Spectral dependence of the photoemission yield for an oxidized CdTe surface gradually covered with In atoms [14].

near the semiconductor and metal surface presented in Fig.4. The YPS experiment will determine E_T and W_{In} . CPD experiment will determine ΔCPD and IPS experiment will determine ϕ_{ss} .

In Fig.5 the change of the spectral dependence of the photoemission yield obtained due to annealing of the CdTe freshly cleaved (110) surface in oxygen atmosphere with pressure 10^{-4} Torr [14] is presented for two different scales: semilogarithmic and linearized due to formula $Y(h\nu) = Y_0 [h\nu - E_T]^{5/2}$. The curves 1 in Fig. 5 were obtained for freshly cleaved surface in UHV ($p=10^{-9}$ Torr). The sticking coefficient of the oxygen atoms to the CdTe surface (high contribution of ionic bonding in CdTe crystal) is small and the annealing process was performed in the relatively high pressure $p = 10^{-4}$ Torr. The curves 1 - 8 correspond to the various exposure times of CdTe (110) surface to the oxygen with pressure $p = 10^{-4}$ Torr. The curve 8 can be treated as corresponding to the saturated of oxygen stable annealed surface. The measured change of threshold energy E_T corresponds to the change of electron affinity and was caused by the dipole layer created on CdTe (110) surface under oxygen adsorption as on the surface the tellurium oxides phase is created [14].

This way prepared surface was used as a substrate to investigate the deposition of the In atoms. The small deposition of In atoms on oxidized CdTe (110) surface leads to the change of the affinity of the photoemitted

electrons as it is presented for curves 0.0 and 1.3 in Fig 6. This change of affinity was not observed for the deposition of less reactive Ag atoms than the In atoms. With the increase of the Indium atoms deposition the contribution of the current photoemitted from the metal increases. For In thickness equal 2.5 monolayers the work function reaches the saturation value of In work function corresponding to the value 3.99 eV well determined for coverage of 50 monolayers. From the set of curves presented in Fig.6 the parameters W and E_T were determined (see insert of the Fig.6). When the surface of CdTe is not oxidized the deposition of the In is not causing the change of the electron affinity [15].

The yield photoemission measurement showed that the deposition of the atoms on the surface of the CdTe leads to the change of the affinity and the surface potential.

The yield photoemission spectroscopy was found as a very sensitive method to indicate the change of the electronic states in the energy region corresponding to the band gap or to the edge of the valence band for surface and near to the surface region. The precise and computerized counting system of the photon and electrons gave the possibility to detect the yield in the range of 8 orders of magnitude [15,16].

Proper choice of the crystal and introduced to it atoms gives the hope of the possibility to influence and to get the electronic structure at the surface region proper for some purposes as well as to get some conclusions for the engineering of new electronic structure materials using e.g. implantation, molecular beam epitaxy or diffusion technique.

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