SURFACE RELATED ELECTRONIC STATES ON CdTe(110) OBSERVED BY MEANS OF OPTICAL SPECTROSCOPY

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Surface differential reflectivity together with photoemission and Auger electron spectroscopies have been applied to observe and identify optical transitions among surface related states on CdTe(110) surfaces. The strongest contributions to the band of optical transitions have been revealed at the photon energies of 2.8, 3.4, and 3.9 eV. Their correspondence to excitations from the occupied $S1$ band to the unoccupied $U1$ one at the Γ, X and X' points of the surface Brillouin zone is discussed.

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Recent invention of the growth techniques of II–VI films on III–V [1] or Si [2] substrates and emerging projects of optoelectronic devices based on wide gap II–VI compounds directly implanted into Si- or III–V-based electronic circuits considerably intensified investigations of II–VI semiconductor electronic structures. Particular interest is focused on their atomic and electronic surface structures. CdTe is one of the most popular subjects of the studies [3–14]. Apart from the classic optical and transport measurements the most advanced experimental methods were applied to acquire detailed information about its bulk and surface electronic structure. The photoemission measurements [3–8] gave almost a complete scheme of the occupied bulk states. The results of theoretical calculations [5, 6, 9–11] generally fit well the experimental data. In spite of charging effects which make such measurements impossible for undoped, as-grown CdTe of the high resistivity, some data on the empty surface states have also been obtained (for Ga-doped n-type crystals) by means of k-resolved inverse photoemission spectroscopy (KRIPES) [13]. Some complementary information was deduced from electron energy loss spectra [14].

In this paper we report our contribution to the investigation of CdTe surface properties. The CdTe(110) surface, cleaved under UHV conditions, was studied *in situ* by means of surface differential reflectivity (SDR), ultraviolet photoemission (UPS) and Auger electron (AES) spectroscopies. We applied SDR spectroscopy as a tool for determination of energy gaps between occupied and empty states.

It gives direct information about the relative position of the states, both known and unknown from other experiments. This helps us to put all previously acquired data on a common energy scale (although excitonic effects should be taken into account [15]) and gives some independent information about the electronic structure of a surface. Moreover it is a contactless technique. Thus, we were able to avoid difficulties connected with the high resistivity of the crystal and the ohmic contact fabrication technology. Applying *in situ* all the methods listed above we were able to study at the same time the energy gaps among surface electronic states as well as the oxidation process, which is the basic procedure in an SDR experiment. Thus, in addition to the information about the surface electronic structure which we obtained, the results reported can be relevant to passivation processes investigations, important for possible future applications of CdTe.

The experiments were carried out in a UHV Vacuum Generators VG-450 system (basic pressure $p = 5 \times 10^{-10}$ torr) working in Istituto di Struttura della Materia in Frascati. The set-up was equipped with a low-energy electron diffraction (LEED) facility, He-lamp, electron gun and a hemispherical electron energy analyser for UPS and AES. A CaF_2 window enabled us to perform the SDR experiments. The pressure in the chamber was measured with an ion gauge. The chemical composition of the atmosphere was monitored by a quadruple mass spectrometer. A UHV preparation chamber attached to the system was used to prepare clean CdTe crystal surfaces. The samples were cut out of undoped p-type CdTe monocrystals grown by a modified Bridgman method in the Institute of Physics, Polish Academy of Sciences in Warsaw and oriented by X-ray diffraction. The samples (parallelepipeds of $4 \times 5 \times 10$ mm dimensions) had the 4×5 mm face parallel to (110) planes with ⟨110⟩ and ⟨001⟩ directions along the edges. They were cleaved along the ⟨001⟩ direction by means of two wedges of different angles (30° and 60°). A 1×1 surface structure was revealed by LEED.

The normal incidence SDR spectra were measured with a cross double beam reflectometer [16]. The signal beam was focused on the CdTe sample cleaved under UHV conditions while the reference beam was reflected from a dummy sample. The intensities of the beams were measured with an optical multichannel analyser with a 0.06 nm resolution in the available wavelength range of 200–1200 nm. The cleanliness and quality of the surfaces investigated as well as the course of oxidation of the surface, were checked and controlled by means of ultraviolet photoemission and Auger electron spectroscopies.

Figure 1 shows the set of SDR spectra sequentially measured for CdTe(110) surface exposed to oxygen. The first reflectivity spectrum was recorded for the clean, freshly cleaved surface. Then the relative change in reflectivity: $\Delta R/R = (R_{\mathrm{clean}} - R_{\mathrm{ox}})/R_{\mathrm{ox}}$ was plotted for every stage of the oxidation process. As it was shown for Si and several III–V compounds [17, 18], oxidation strongly influences electronic surface states and quenches optical transitions involving them. Consequently, it was proved [18] for compounds of the energy gaps similar to that of CdTe that $\Delta R/R \approx dA\varepsilon_s''$ for a large part of the photon energy range available in the experiments reported (d being the thickness of the oxide monolayer, A — the quantity depending on the bulk properties and ε_s'' — the imaginary part of the
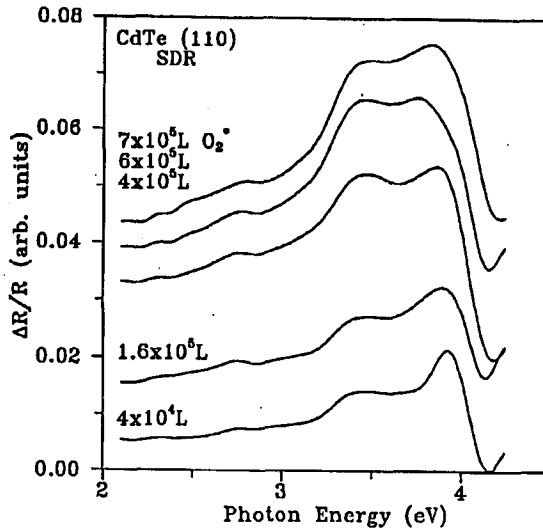
Fig. 1. Evolution of the SDR spectra as a function of oxygen exposure. The oxidation was activated by a hot filament of the ion gauge placed in line-of-sight of the surface.

surface dielectric function). Thus, we can assume that the curves in Fig. 1 show the essential features of the spectrum of optical transitions among surface related states.

The last curve, corresponding to the saturated changes in the surface optical properties, was deconvolved into three Gaussian singlets (Fig. 2A). They occur at 2.8, 3.4, and 3.9 eV. At similar result was obtained for the corresponding curve recorded for another cleave of the sample (2.8, 3.4, 3.8 eV, see Fig. 2B). At last, the spectrum measured with polarised light were deconvolved into the singlets centred at 2.8, 3.4, 3.9 eV (Fig. 2C). The differences between the relative heights of the singlets observed in the spectra shown in Fig. 2 are connected with deviations from the perfect surface structure. Similar effects were revealed in photoemission studies of CdTe(110) surfaces [5, 21]. The energy positions of the singlets correspond well to the width of energy gaps between $S1$ (the highest occupied) and $U1$ (the first unoccupied) bands at the Γ, X and X' points of the surface Brillouin zone, respectively. The widths of these gaps were estimated from the energy positions of the surface states observed by the angle resolved ultraviolet photoemission spectroscopy (ARUPS) [6–8] and KRIPES [13]. Nevertheless, we have to take into account that the transition energies deduced from the reflectivity experiment can differ from the band gaps estimated on the basis of the one-electron band scheme because of excitonic effects and, also, due to shifts of reflectivity spectra features with respect to absorption maxima. The latter ones can be estimated from the Kramers–Kronig analysis of SDR data. Such a procedure performed for some III–V compounds [17, 18] showed that the assumption $\Delta R/R \approx dA\varepsilon_s''$ can lead to the shift of ε_s'' features by 0.1–0.2 eV. The similar procedure for the CdTe SDR spectra is in progress.
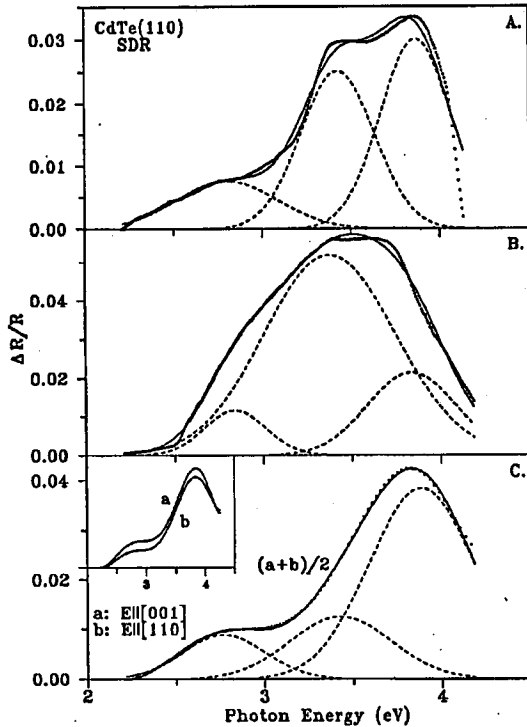
Fig. 2.   The SDR spectra deconvolved into Gaussian singlets; (A) the last spectrum (for 7×10^5 L, 1 L= 10×10^{-6} torr) from Fig. 1; (B) another cleave of CdTe(110) (compare Ref. [19]); (C) the curve obtained from the measurements with polarised light [20]. The comparison of the curves a and b (see the inset) clearly shows that the optical anisotropy of the surface investigated is small and almost independent from the photon energy.

The SDR experiments performed for the cleaved and then gradually oxidised CdTe(110) surfaces enabled us to observe optical transitions between occupied and empty surface states and propose their possible positions in the surface Brillouin zone.

The lack of strong optical anisotropy of CdTe(110) suggest that the maxima revealed in the spectra correspond to transitions occurring at similar energies over substantial parts of the surface Brillouin zone. Nevertheless some influence of other surface and bulk related phenomena on surface optical properties of CdTe(110) still have to be taken into account.

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