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Laser-induced band-bending variation on room-temperature CdTe(110)1 × 1 surfaces observed in photoemission and through the Franz-Keldish effect in surface differential reflectivity

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A laser-induced band-bending variation on ultrahigh vacuum cleaved CdTe(110)1 × 1 surfaces kept at room temperature has been observed both in angle-resolved photoelectron spectroscopy (ARPES) and, through the Franz-Keldish (FK) effect, in surface-differential reflectivity. Through ARPES spectra, the shift of the Fermi level, between the sample obscured and illuminated with an Ar^+ laser power of 500 mW has been determined to be 0.2 eV. The FK effect has been observed at the E_0 bulk critical point and studied as a function of laser power, showing a linear increase in its oscillation amplitude up to a power of 400 mW. Upon switching off the laser, the FK effect disappears exponentially with a time constant of about 1300 s. A surface photovoltage induced by the helium lamp has also been observed.

I. INTRODUCTION

The interest in studying II-VI compounds has increased in the past few years since they can feature band gaps ranging from the near ultraviolet to the far infrared. Among the II-VI compounds CdTe is the one most studied not only for its interesting optical and electronic properties, but also because with its zinc-blende structure and its 1.56-eV wide direct band gap, it is the basic compound of a double family of alloys of the form $Cd_{1-x-y}Hg_xMn_yTe$, interesting as tunable high-efficiency infrared detectors.[1] Since the quality of such detectors strongly depends on the quality of the substrate used for the growth, the substrate must be well characterized and with very low impurity levels in order to reduce the possibility of contamination of the epitaxial layers.

Previous publications[2] have shown that Schottky-barrier heights at Au-CdTe and Sb-CdTe interfaces depend strongly on the choice of the chemical etchant used to prepare the surface prior to metallization. Schottky-barrier heights have been usually measured with photoemission from the valence band and from core levels.[3] However, the work function of a semiconductor may be changed by the absorption of light.[4–6] The difference of the work function measured under illumination and in the dark is the so-called surface photovoltage (SPV). In this context, it has been shown in recent years that great care must be used for a good evaluation of Schottky-barrier heights from photoemission data due to the presence of beam-induced SPV.[6] The best way to evaluate beam-induced SPV is to measure it directly. A Kelvin probe has been combined with photoemission thus allowing the measurement of the beam-induced SPV.[7,8] However, some restrictions are present in such experiments: the angle between photoemission beam and sample must be very close to the grazing one; the photoemission current is also illuminating the Kelvin electrode and might affect the contact potential difference (CPD) measurement. To overcome these difficulties CPD measurements can be performed after SPV has been induced by a photoemission beam, by rotating the sample, i.e., between the sample illuminated by the synchrotron beam and the sample obscured.[9] However, also in this case the experiments must be restricted to study barrier heights where the metal and the semiconductor have a similar work function. In fact, in the case of metal islands on a semiconductor, we can, reasonably, assume that a Kelvin probe measures some kind of averaged work function. This is due to the large electrode area (few millimeters) that probe simultaneously the metal islands and the semiconductor free regions, unless one uses a micro-Kelvin probe with a very thin electrode (few nanometers), that might probe different areas on the same sample. In this way photoemission results on the system Ag/GaP(110) [Ag and *n*-type GaP(110) have similar work function] could be corrected for the induced photovoltage by measuring the contact potential difference between the sample illuminated by the synchrotron beam and the sample obscured. In the general case this averaged work function is neither the semiconductor one nor the metal one and will depend on coverage and islands extension.

Also the Franz-Keldish (FK) effect[10,11] gives the possibility of measuring Fermi-level movement as a function of oxygen exposure or metal evaporation.[12–14] The advantage of such a method over the Kelvin probe is that, in the case of metal islands on a semiconductor, the FK effect is induced only from the areas of the surface where the metal has adsorbed, i.e., those places where the local band bending has changed. The areas of the surface which are metal-free give no contribution to the FK effect: in this way we get rid of work-function inhomogeneity in nonuniform metal/semiconductor interfaces. In this context every kind of metal can be used on any semiconductor regardless of their work function.

Using the FK effect no absolute value of band bending can be directly measured, but differences and variations in band bending may be determined with excellent precision and without disturbing the surface by the measurement itself.

In this paper we present laser-induced band-bending variation on ultrahigh vacuum cleaved CdTe(110)1 × 1 surfaces kept at room temperature, observed with angle-resolved photoelectron spectroscopy (ARPES) and, through the FK effect, with surface-differential

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reflectivity (SDR). Through ARPES spectra, the shift of the Fermi level between the sample obscured and illuminated with an Ar^+ laser power of 500 mW has been determined to be 0.2 eV. The FK effect has been observed at the E_0 bulk critical point and studied as a function of laser power, showing a linear increase in its oscillation amplitude up to a power of 400 mW. Upon switching off the laser, the FK effect disappears exponentially with a time constant of about 1300 s. A surface photovoltage induced by the helium lamp has also been observed.

II. EXPERIMENTAL SETUP

The undoped, *p*-type CdTe crystals were grown by a modified Bridgman method at the Institute of Physics, Polish Academy of Sciences in Warsaw. Free-carrier concentration was below 10^{16} cm^{-3}, the acceptor level being attributed to Te vacancies. The samples (parallelepipeds of $4\times5\times10$ mm^3 dimensions) were oriented by x-ray diffraction. The 4×5 mm^2 face was parallel to (110) planes with the [110] and [001] directions along the edges. The samples were cleaved along the [001] direction by means of two wedges of different angles (30° and 60°) in an UHV preparation chamber attached to the main chamber. This procedure gave us mirrorlike surfaces of a 1×1 structure, as checked by low-energy electron diffraction (LEED).

Angle-resolved photoemission spectra were recorded in an UHV Vacuum Generators VG-450 chamber at a pressure of less than 2×10^{-10} Torr. The chamber was equipped with facilities for auger-electron spectroscopy and LEED. Unpolarized 21.2-eV radiation from an ultraviolet (UV) helium discharge lamp was used. The estimated total-energy resolution as determined by the analyzer voltages and the width of the He I light was 150 meV.

The optical experimental setup consists of an ion Argon laser (5500 A Ion Laser Technology, laser radiation between 457 and 514.5 nm) used to give raise to a band bending with the consequent observation of the FK effect and ARPES on the clean surface. The laser was incident on the sample with an angle of 30° off the normal to the surface while its intensity was varied in the range 10–500 mW to investigate its influence on the FK line shapes. A spherical lens was used to shape the beam so that the beam illuminated area on the sample was about 5×5 mm for the FK effect and ARPES.

The method of SDR has been used to observe the FK effect. SDR consists in shining light at normal incidence on a freshly cleaved CdTe(110) surface and measuring the reflectivity normalized to a dummy sample. The light emitted from a 150-W lamp passed through a lens and is separated into two beams through a semitransparent CaF_2 beam splitter. One beam (I) is focused through another lens on the surface into the UHV chamber while the second beam (Io) is focused onto an aluminum mirror. The light then enters an EG&G PARC half-meter monochromator with an optical multichannel analyzer (OMA) mounted on the exit slit. The intensities of the two reflected beams are measured by the OMA that is computer controlled through an IEEE 488 interface. The emission lines from a Hg lamp were used to calibrate the wavelength response of the spectrometer to within 1 meV for emission near the band-gap energy of CdTe. The data stored are the values of the ratio between the reflectivity of the cleaved surface and the reflectivity of the dummy sample, normalizing with respect to the background signal through four compouter controlled shutters. A 600-nm long-wavelength pass filter is used to cut out laser light reflected off the sample and to get rid of higher orders of the monochromator.

The spectra were measured when the laser was off (R_0) and during irradiation with the laser [$R_1(P)$]. The rela-

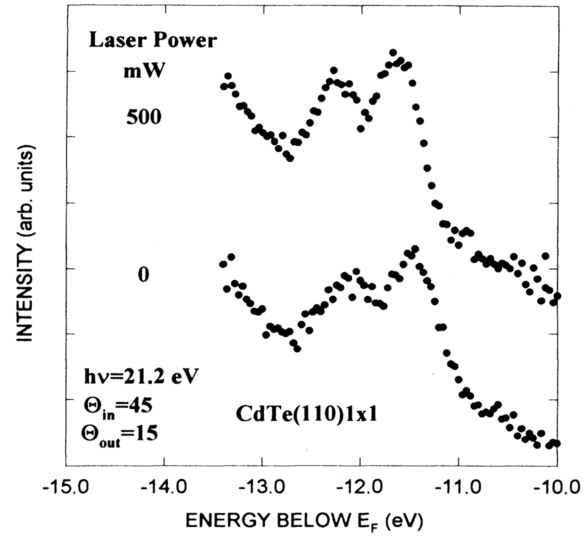

FIG. 1. ARPES spectra showing the Cd 4*d* level without laser illumination (lower curve) and with a laser illumination of 500 mW (upper curve).

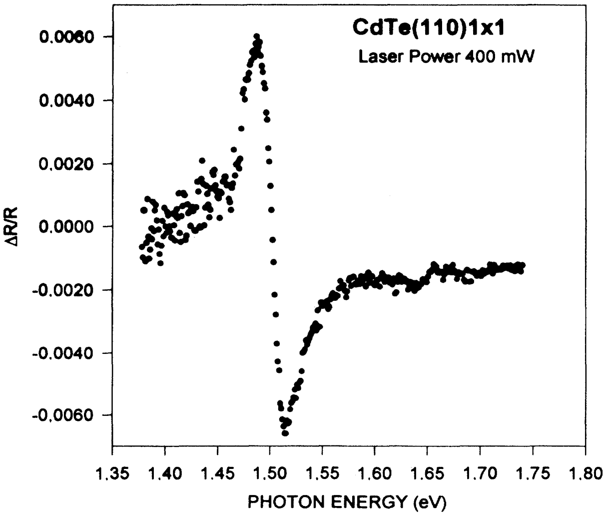

FIG. 2. Reflectivity variation brought about by laser irradiation of the sample with a power of 400 mW.

tive change in reflectivity

$$\Delta R/R=[R_1(P)-R_0]/R_0 \qquad (1)$$

could be determined for every stage of the laser power P. When the sample is irradiated by the laser beam, a photovoltage at the surface is induced with a consequent band bending in the space-charge region. This implies a change of the surface electric field during laser irradiation. Therefore, when measuring $\Delta R/R$ a change in the bulk optical properties induced by the change of the surface electric field is, in principle, to be expected. This is indeed the basis of electroreflectance spectroscopy,[15] in which a modulated external field applied normal to the surface gives rise to a reflectivity signal. In this way oscillatory features[16,17] with maxima (or minima) corresponding to critical points of the bulk band structure are observed. The higher the electric field is, the larger the FK oscillations are.

In our experiment we use a p-doped sample so that the Fermi level (FL) should be close to the valence-band maximum. Upon irradiating the surface with the laser, the FL postion at the surface will move towards a new neutrality level closer to the midgap position. ARPES spectra will then show a shift towards higher binding energy while FK oscillations will appear in correspondence to bulk critical points and their amplitude will increase with laser power. The parabolic bulk critical point E_0 around 1.5-eV photon energy has been chosen in our experiment in order to get rid of contribution from the laser light in the reflectivity spectra.

III. EXPERIMENTAL RESULTS

Figure 1 shows the Cd 4d core level as observed in ARPES with the laser off and with a power of 500 mW. As expected, a shift towards higher binding energy of 0.2 eV is clearly visible in the ARPES spectrum taken with $P=500$ mW (upper curve), as respect to the spectrum taken with the laser off (lower curve).

Figure 2 shows the change of reflectivity upon irradiating the sample with a laser power of 400 mW. A FK oscillation is clearly visible around 1.5-eV photon energy with an amplitude of 1.3% and with a shape in accordance to that found by Cardona, Shoklee, and Pollak[15] Figure 3 shows a complete set of $\Delta R/R$ spectra for laser power between 100 and 500 mW. The shape of the FK oscillation does not change with laser power. Figure 4 reports the amplitude of FK oscillation for every laser power. As visible, the oscillation amplitude increases linearly up to a laser power of 400 mW while a faster increase is observed for higher laser power. The linear trend is in accordance with the calculation of electric-field-induced changes in $\Delta R/R$ at a parabolic point edge.[18] The maximum FK amplitude (2.5%) is observed for a laser power $P=500$ mW and coresponds to the 0.2-eV shift observed with ARPES. The data points of Fig. 4, then, represent the movement of the FL at the surface with a maximum shift of 0.2 eV towards bulk midgap.

After turning the laser we have measured the variation of the FK amplitude and the data points are reported in Fig. 5. The FK amplitude tends to decrease quite slowly: the experimental points are well described by an exponential decay (full line) with a time constant of 1300 s. Such a long discharging time indicates the existence of traps, in the band-bending region near the surface, for the electron-hole pairs generated by the laser light.

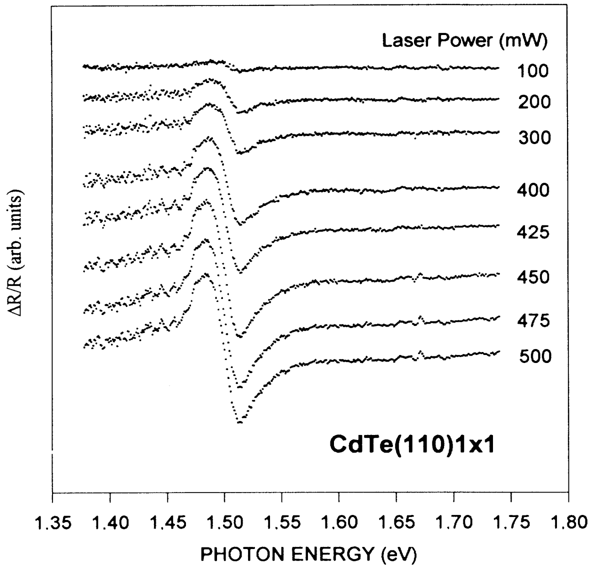

FIG. 3. Reflectivity variation brought about by laser irradiation of the sample with laser power between 100 and 500 mW.

Finally, the surface was illuminated with the UV lamp for 30 min while the laser was off. The UV lamp was then switched off and the sample was positioned for reflectivity measurements. Five minutes after switching off the lamp we got a reflectivity signal ($R_{t=0}$); after 20 and 60 min the reflectivity was measured again (R_t) and the DR/R variation is reported in Fig. 6. We observed

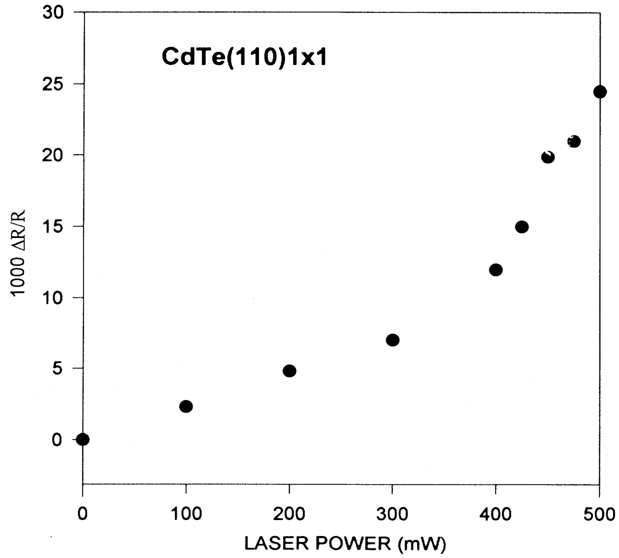

FIG. 4. FK oscillation amplitude for laser power between 100 and 500 mW.

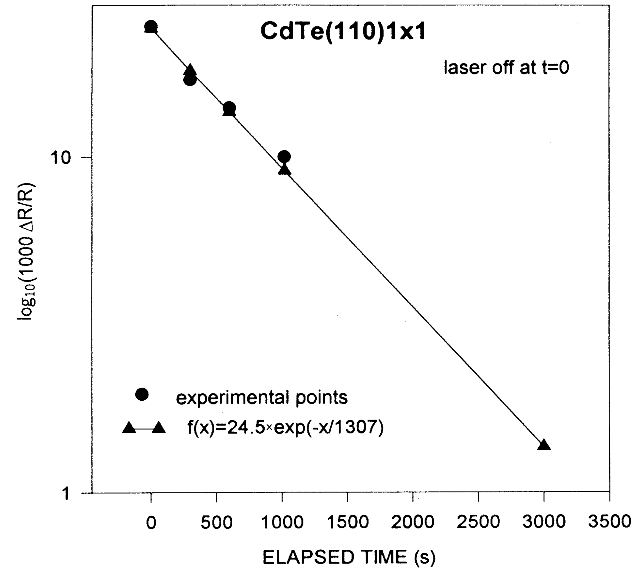

FIG. 5. Variation of the FK oscillation amplitude after turning off the laser with an exponential decay fit (full line).

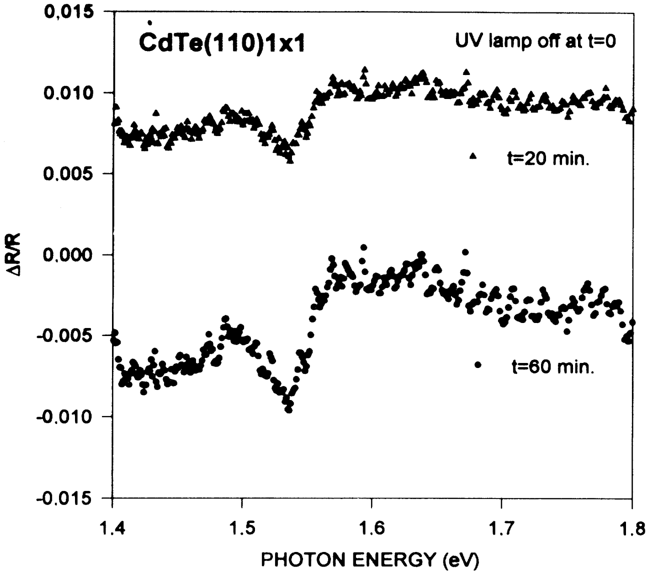

FIG. 6. Reflectivity variation brought about after turning off the UV lamp (at time $t=0$). The reflectivity variation is $\Delta R/R = R(t=0)/R(t)-1$.

at FK oscillation with an amplitude of 1% that indicates that photovoltage is also induced by the UV lamp. A comparison with data in Fig. 4 indicates that such shift is quite small (~80 meV) but not negligible.

IV. CONCLUSIONS

In conclusion we have measured the Franz-Keldish effect on the clean CdTe(110)1×1 surface as a function of an Ar^+ laser power. A linear increase in the FK amplitude has been observed up to 400-mW laser power. The discharging time has been measured to be of the order of 40 min. A photovoltage induced by the helium lamp has been revealed through the FK effect. The method seems to be promising for studying the formation of metal/semiconductor interfaces.

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