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Work function and photoemission studies of cesium-coated CdTe(100)

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The work function and photoemission from p-type CdTe(100) single-crystal phosphorus doped to $\sim 10^{15}$ cm^{-3} and crystals that were subsequently highly doped to $\sim 10^{19}$ cm^{-3} with Li and covered with submonolayers of Cs were studied. In some instances the cesium-coated surfaces were modified by deposition of oxygen. Large work-function changes were found in CdTe at the initial deposition stages of Cs indicating the formation of large dipole moments on the CdTe(100) substrate. Band-gap-limited (at 1.56 eV) long-wavelength photoemission was observed from the above samples. The total spectral photoemission for visible and near-infrared regions was determined.

INTRODUCTION

Negative-electron-affinity (NEA) -based photoemitters have been of great interest for the last two decades.[1] In photoemitters, a state of zero or negative effective electron affinity changes the principal mode of electron transport from "hot electron" mode, with a short mean free path and a related small ($\sim$250 Å) escape depth, to a "cold electron" minority-carrier diffusion mode (escape depth: $\sim 10^4$ Å). Extensive studies have been reported on Si(Cs-O) and on systems of the III-V group semiconductors, such as GaAs(Cs-O), InP(Cs-O), and GaP/Cs. These systems are characterized by a photoemission threshold near the band-gap energy. Some of the ternaries of the III-V group, $In_{1-x}Ga_xAs$(Cs-O) and $In_{1-x}As_xP$(Cs-O), were studied with the goal of adjusting the band gap for the specific type of application. The use of the ternary III-V compound semiconductors allows us to shift the onset for efficient photoemission toward the infrared region of the spectrum and excellent detectors in the near infrared were constructed.[2] There is also a third group of infrared detectors based on the II-VI compounds, CdTe and $Hg_{1-x}Cd_xTe$. These materials form high-quality systems (the lattice mismatch between CdTe and $Hg_{1-x}Cd_xTe$ is only 0.3%) which have great potential applications in the field of photoelectronic devices operating at wavelengths longer than those obtainable with the III-V semiconductors.[3,4] CdTe has an energy band gap of $E_g = 1.56$ eV, which is very suitable for obtaining NEA after appropriate surface treatment. In the past, CdTe has not been explored because it was difficult to obtain high p-type doping ($\sim 19^{19}$ acceptors/cm^3) levels necessary for a narrow band bending.[5] The space charge required for band bending is provided by ionized acceptors in the surface region. Recently, preparation of highly p-type-doped ($2\times10^{17}-\sim10^{19}$ cm^{-3}), good quality CdTe was reported[6–10] making it possible to obtain NEA photoemitters. As far as we know only one attempt to activate CdTe to NEA has been reported.[7]

In this paper we report the observation of near-infrared photoemission from CdTe/Cs.

EXPERIMENT

Low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), work-function dependence on Cs coverage, and photoemission yield spectroscopy were employed in this investigation.

The samples used were p-CdTe single crystals, grown by the vertical Bridgman method [oriented to within ±0.5°, in the (100) direction]. The samples had p-type bulk carrier densities of 2×10^{15} cm^{-3}. This value was measured by the Hall effect, C/V and I/V techniques.

The preparation of the (100)-oriented surfaces was done by mechanically polishing of the single crystal with 0.3-μm aluminum oxide. The sample was subsequently rinsed with deionized water, and then cleaned with trichlorethylene, acetone, and methanol in an ultrasonic cleaner. Finally, prior to insertion into the UHV chamber, the surface was etched with a solution of bromine in methanol (2% in volume) to remove the uppermost layer.[11] These surfaces were subsequently sputter-cleaned *in situ* by means of an Ar^+ ion beam of 800 eV and thermally annealed to 250 °C for 5 min. In the majority of cases, such a procedure gave a well-defined CdTe(100)(1×1) LEED pattern with no traces of impurities (as monitored by AES). The surface treatment, modification, and characterization was performed in an ultrahigh-vacuum systems (6×10^{-11} Torr, base pressure) equipped with a LEED retarding grid detector, AES and electronics for the measurement of the work-function changes by a retarding field method[12] with a ±50-mV resolution. The experimental system also allowed admis-

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sion of controlled amounts of molecular oxygen (O_2) to the sample. The photoemission measurements were performed using a high-pressure Hg lamp (200 W) and a grating monochromator (Durham) with a resolution of $\Delta h\nu \sim 0.006$ eV. The experimental arrangement was described elsewhere.[13,14] Cs and Li were evaporated from SAES getters, each thoroughly outgased and enclosed in a cell made of stainless steel with a hole covered by a rotatable shutter. The background pressure during alkali deposition was kept below 10^{-9} torr. The Cs coverage was monitored by AES. Throughout this work we will define a Cs monolayer (ML) as 4.6×10^{14} atoms cm^{-2} which is close to the density of a saturated Cs monolayer on most metals and semiconductors.[15–17]

RESULTS AND DISCUSSION

Figure 1 shows a typical cesium (Cs_{MNN} 536 eV) Auger peak-to-peak plot versus deposition time obtained during growth of the layer on the substrate kept at room temperature. From the intensity of the Cs_{MNN} signal a nearly constant sticking coefficient (s) is obtained for coverages up to $\theta \cong 0.2$ (deposition time $\sim$4 min). Above this coverage a second region with increasing s is obtained up to the break in the curve which is attributed to completion of the first monolayer (deposition time $\sim$10 min). Above $\theta=1$ the slope of the curve becomes significantly smaller indicating a drastic reduction of the s value. A similar behavior was observed at the initiation of each new Cs layer deposited on GaAs(110) (Ref. 16) and also was attributed to a low s value for this initial condensation of Cs atoms on top of existing two-dimensional (2D) clusters consisting of Cs atoms.[15] The growth of Cs by the formation of 2D clusters which coalesce near a monolayer coverage is consistent also with the absence of any ordered LEED structures. This type of growth is assumed to exist in our case, too.

Work-function changes versus cesium coverage (θ) of a CdTe(100) surface are shown in Fig. 2. The curve exhibits a fast initial drop, $d(\Delta\phi)/d\theta_{Cs} \approx 21.7$ eV/ML, up to $\theta=0.06$, followed by a more moderate decrease and a plateau beyond $\theta=0.335$. From the Helmholz equation, $\mu=(\Delta\phi\times10^{18})/(2\pi n_{Cs}\times300)$, the dipole moment per

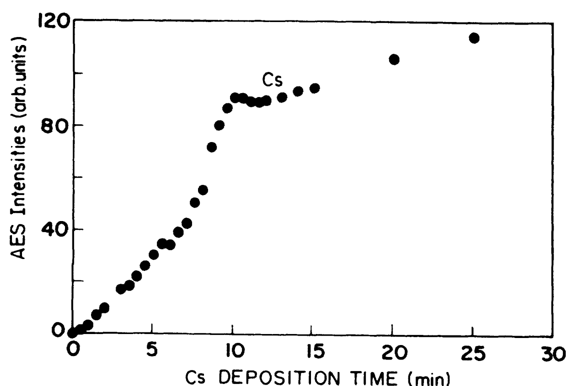

FIG. 1. Intensity of the AES signal (peak to peak) as a function of Cs deposition time.

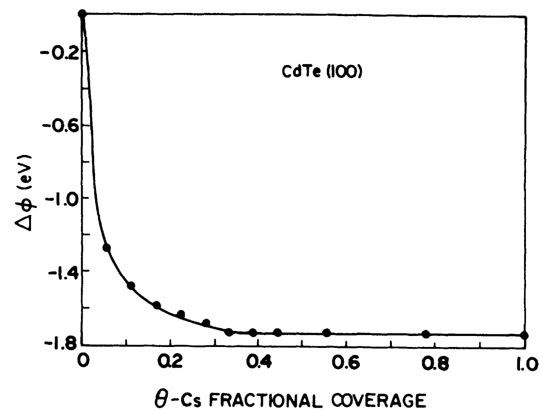

FIG. 2. Work-function lowering of CdTe(100) as a function of Cs surface coverage.

adsorbed cesium is calculated from the initial slope of the curve as $\sim$25 D, where $\Delta\phi$ is given in eV and n_{Cs} is the number of adsorbate atoms/cm^2. Cesium is most probably ionic at low coverages on this surface. This dipole moment is higher than values typically reported for Cs on metal surfaces (4–15 D).[18,19] The high dipole moments obtained on semiconductors were interpreted, for GaAs,[20] as caused by a longer effective dipole length. This arises from less effective screening of the Cs^+ charge by electrons in the bulk. The high value of μ obtained indicates practically complete transfer of the Cs valence electron to the adsorbent at low surface coverage. This effect is, however, rapidly suppressed with increasing n_{Cs}. The nonlinear variation of $\Delta\phi$ with coverage can be described in the simplest way by a point depolarization model as developed by Topping.[21] According to this model $\Delta\phi$, the lowering of the work function is given by

$$-\Delta\phi=4\pi\mu_0 n_{Cs}/(1+9\alpha n_{Cs}^{3/2})\ , \tag{1}$$

where n_{Cs} as above is the density of adsorbed atoms, μ_0 is the dipole moment at infinite dilution, and α is the adsorbate effective polarizability. Using this model a value of $\mu_0=64$ D was calculated for the very initial stages of Cs adsorption. Even higher μ_0 values were found by Clemens, von Wienskowski, and Mönch for Ge(111) and GaAs(110).[22] The dipole moments calculated from the initial slopes of the $\Delta\phi$ versus θ curves were as high as 220 and 48 D for GaAs/Cs and Ge/Cs, respectively. The difference between the dipole moment calculated from Helmholz equation and Eq. (1) stems from the fact that in the first case an average value of μ is obtained. The Toppings model gives a value for the dipole moment extrapolated to zero coverage where no mutual depolarization of the aligned dipoles exists and the electron charge transfer from Cs to the CdTe substrate is maximum.

Already in the early days of NEA research it has been realized that the replacement of a simple Cs monolayer on the emitter surface by a more complex and thicker layer of Cs and Cs oxide lowers further the electron affinity. The biggest emphasis with NEA cathodes is to lower the potential barrier at the surface of the semiconductor as far as possible, since this determines the

minimum threshold of response to photon energy. The lower the potential barrier at the surface, the lower the band gap can be made while the NEA property is still preserved.

An extensive literature exists on this subject:[1,2,23] With III-V semiconductors, oxygen treatment of cesium-coated surfaces is often performed and alternative layers of Cs and oxygen are being deposited. This treatment not only improves the photoemission yield and shifts the threshold frequency to lower photon energies, but also improves the long-term stability of the photoemitter.

In our case exposure of the CdTe surface to oxygen for 30 min at a pressure of 6.6×10^{-8} Torr and subsequent deposition of 0.5 ML's of Cs lowered the work function by 2.20 eV (Fig. 3), the dependence of $\Delta\phi$ versus deposition time of Cs being similar to the oxygen-free sample. On further exposure to O_2 (20 L) the work function of the cesium-coated sample increased by 0.5 eV from its minimum value. Additional exposure to O_2 had practically no influence. On subsequent deposition of cesium a further lowering of the work function to 2.45 eV was obtained. These results were obtained for the highly doped *p*-CdTe(100) substrates which were subsequently employed in the photoemission measurements.

The results of the work-function measurements as obtained by the diode method represent average values. It is very plausible that on the surface of doped CdTe regions exist where the work function is substantially lower and these contribute mainly to the photoemission process.

Photoemission measurements were performed on two types of samples: samples which were phosphorus doped ($\sim1\times10^{15}$ cm^{-3}) during growth, and samples that were subsequently doped *in situ* ($\sim1\times10^{19}$ cm^{-3}) by surface diffusion of Li in the UHV chamber.[6] Photoresponse during cesium deposition was observed from the phosphorus-doped samples below the cesium threshold wavelength, $\lambda_{Cs}\approx635$ nm. The same is true for the non-cesium-coated Li-doped samples. The highly Li doped cesium-coated samples showed a very definite photoelectric emission at wavelengths longer than λ_{Cs}. Photoelectric emission was obtained at very low Cs coverage only. Figure 4 shows photoemission currents as a function of

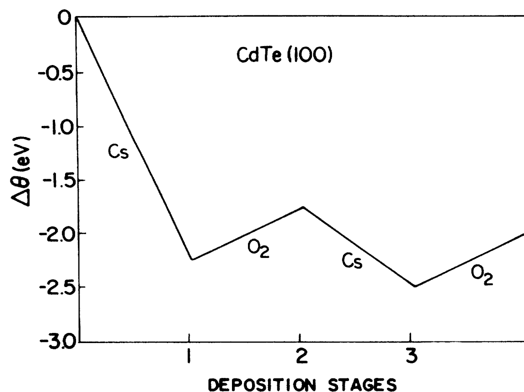

FIG. 3. Work-function change of CdTe(100) on Cs and O_2 deposition.

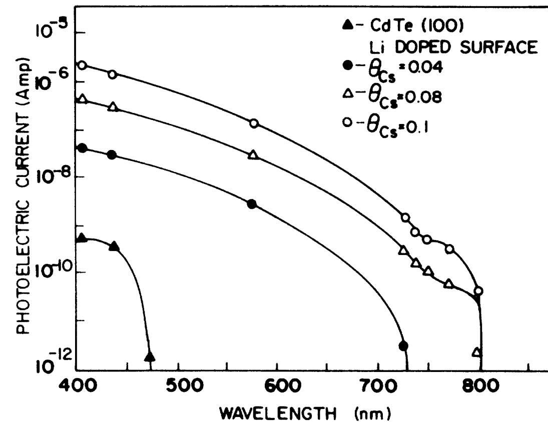

FIG. 4. Photoemission current of Li-doped *p*-CdTe(100) as a function of incident radiation wavelength for the uncoated substrate, and for different Cs coverages.

wavelength, for highly Li-doped clean, and cesium-coated CdTe samples. For $\theta_{Cs}=0.04$, photoemission with a threshold wavelength at 730 nm was obtained. For $\theta_{Cs}=0.08-0.1$ the photoemission was nearly two orders of magnitude higher than for $\theta_{Cs}=0.04$, the threshold wavelength being shifted to 800 nm for both surface coverages. Further cesium coatings resulted in much lower photoemission. Comparing our data for the two sets of samples (medium phosphorus and highly *p*-type Li doped) we note that $\lambda_{th}=800$ nm obtained for *p*-CdTe (100) correlates with the band gap of the semiconductor ($E_g=1.56$ eV) indicating that NEA was obtained with the highly *p*-doped CdTe/Cs (consistent with the high dipole moment obtained at the very initial stages of Cs coverage).

The calculated quantum efficiency was low and ranged from $\sim5\times10^{-3}$ for a wavelength of 400 nm to $\sim5\times10^{-7}$ for wavelengths near λ_{th}. Such a low quantum yield may be explained by a number of causes.

As was already stressed, most probably only a fraction of the surface has a work function low enough to give photoemission in the spectral region investigated. Secondary-ion mass spectroscopy measurements indicated that a substantial fraction of the surface has a Li concentration above the value calculated from the doping level. This together with a slightly disordered CdTe(100) surface—as inferred from the LEED pattern—most probably contributes a high density of defects in the surface region. These defects may act as trapping and recombination centers for the electrons in their movements to the semiconductor-vacuum interface.

In conclusion, our preliminary investigations demonstrate that CdTe can be activated to give negative electron affinity. This is due to the very high *p*-type doping ($\sim10^{19}$ acceptors/cm^3 necessary for the narrow band bending) and subsequent deposition of Cs.

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