PHYSICAL REVIEW B VOLUME 40, NUMBER 5 15 AUGUST 1989-I

Metal submonolayers on Hg-Zn-Te alloys: Electrochemical and electrolyte electroreflectance studies

C. Nguyen Van Huong
Laboratoire d'Electrochimie Interfaciale du Centre National de la Recherche Scientifique, 1 place Aristide Briand, 92195 Meudon Principal CEDEX, France

P. Lemasson
Laboratoire des Matériaux Moléculaires du Centre National de la Recherche Scientifique, 2 rue Henry Dunant, 94320 Thiais, France

(Received 18 January 1989; revised manuscript received 3 April 1989)

Electrodeposition of Ag and Cu in the dark at mercury-zinc-telluride alloys (HZT) is studied by electrochemistry and electroreflectance. The specific importance of submonolayer deposits on the behavior of electrolyte-HZT junctions is evidenced. The morphology of the deposits depends drastically on the experimental conditions and especially on the applied potential. Cu and Ag deposits are done in the dark and in underpotential regime like that for metal substrates. However, the electrochemical behavior of these layers is completely different from what is observed with metal electrodes. Electroreflectance spectra recorded with metal-coated alloys present an extremely specific behavior, the spectrum relative to the E_1 transition of the substrate vanishing and a new broad feature being created. This phenomenon is especially important for alloys with composition $0.3 \le x \le 0.7$ whereas for binary alloys such as ZnTe, HgTe, and GaAs it does not exist. A specific chemical interaction between Ag and Cu and the HZT substrate is postulated, based on electrochemical and electroreflectance results, which depends strongly on the chemical composition of the substrate.

I. INTRODUCTION

Up to now, electrochemical metal deposition on semiconductor substrates has been used for several purposes: (i) protection from corrosion of low-band-gap semiconductor electrodes in photoelectrochemical cells,[1] (ii) improvement of efficiency (photovoltage) of solar cells,[2] (iii) catalysis of the hydrogen evolution reaction,[3] and (iv) for obtaining high-barrier metal-semiconductor Schottky junctions.[4]

It is well established from solid-state-physics investigations that the initial steps of metal-semiconductor interface formation, especially in the monolayer range, is of particular importance in understanding the behavior of Schottky barriers.[5] Due to the development of ultrahigh-vacuum surface-science techniques in the last decade, it was possible to establish that metal-semiconductor interfaces are complex and present regions with strong chemisorption and/or diffusion, local charge distribution, and new dielectric properties.[6] For these investigations, growth of the metal layer is generally achieved using a vacuum deposition technique. However, the electrochemical method may appear as an attractive alternative to the previous one due to its particular versatility. Coverage, form, and microstructure of the deposit can be easily monitored by controlling and changing solution composition, time, and potential of deposition as well as mass transport conditions.

Mercury-zinc-telluride (HZT) alloys have been grown only recently, and due to their stability, which is better than that of mercury-cadmium-telluride (HCT), they seem promising materials for production of infrared (ir) detectors and optoelectronic devices.[7] $Hg_{1-x}Zn_xTe$ II-VI alloys crystallize in the zinc-blende structure in the whole composition range ($0 \le x \le 1$), and the lattice parameter obeys Vegard's law,[8] while the E_0 band gap and the E_1 transition lie in the range 0 (-0.14)–2.25 eV and 2.15–3.6 eV, respectively.[8,9]

Preparation of Schottky barriers with good rectifying properties is still a problem with HCT and HZT. In this direction it seems important to study the feasibility of metal electrodeposition on HZT and to investigate subsequently the electrochemical behavior of such modified electrodes. The work function of HZT has not been measured, but that of ZnTe as well as that of HgTe are known.[10] As long as the values of these two work functions are not very different (5.8 and 5.9 eV for ZnTe and HgTe, respectively) it seems reasonable to assume that the work function of p-type HZT lies in the range 5.8–5.9 eV. Therefore Cu and Ag, which are "seminoble" metals with work functions 4.65 and 4.26 eV, respectively,[11] appear to be good candidates for production of Schottky barriers by deposition on p-type HZT.

In the present work, Cu and Ag deposits are prepared electrochemically in the dark. The electrolyte-semiconductor as well as the electrolyte-metal-semiconductor interfaces are studied using cyclic voltammetry, capacity, and electroreflectance (ER) measurements. The latter technique has been used successfully to characterize monolayer and submonolayer metal deposits on metal substrates[12] but, to our knowledge, has been employed only one time to characterize metal deposits on semiconductor substrates.[13]

Submonolayer metal deposits are studied in the present paper and an attempt is made to correlate the experimental results with the structural properties of the metal layer and the chemical nature of the substrates.

II. EXPERIMENT

A. Apparatus and Samples

p-type HZT was grown by the traveling-heater method and kindly donated by Dr. R. Triboulet (Laboratoire de Physique des Solides, Meudon, France). Sample preparation and mounting for electrochemical measurements were already reported.[9] Surface treatment includes mechanical polishing with diamond paste (0.5 μm) and chemical etching in 1% bromine in methanol solution. The electrochemical cell is of the classical three-electrode type with a vitreous carbon counterelectrode and a mercurous sulfate electrode (MSE) as a reference. Electrolytes are prepared from "Suprapur" perchloric acid and ultrapure water (Centre National de la Recherche Scientifique patent) ($0.1M$ $HClO_4$). For metal deposition a low concentration ($10^{-5}M$ to $5\times10^{-5}M$) of $AgNO_3$ or $CuSO_4$ is used. In each case, solutions are deaerated by nitrogen bubbling.

Electroreflectance measurements are performed with a $(0.5\ V)_{rms}$, 15-Hz ac perturbation, in the energy range 2–4 eV with a light beam impinging the electrode surface at near-normal incidence. The complete experimental setup has been described previously.[14]

B. Experimental procedure

After chemical etching, the bare HZT electrode is dipped in the supporting electrolyte ($0.1M$ $HClO_4$), avoiding direct contact with air. The basic properties of the interface that is formed are then determined by measurement of the current- and admittance-versus-potential characteristics and of ER spectra at fixed potential. After this characterization, the HZT electrode is transferred to another electrochemical cell whose electrolyte contains metal salt in order to achieve the metal deposition. The latter operation is done at various deposition potentials V_d and for different times t_d in order that the density and size of metal nucleation germs are varied.

Finally, after careful rinsing with ultrapure water, the coated electrode is dipped back in the first electrochemical cell which contains $0.1M$ $HClO_4$ electrolyte alone. It is worth mentioning that the coated electrode is characterized following a procedure which allows us to have results directly comparable with those obtained at bare electrodes.

The choice of the potential range where the electrode is operated in the supporting electrolyte is done keeping in mind that we are preoccupied with avoiding both anodic and cathodic electrode processes. The former corresponds to electrode oxidation and anodic dissolution and the latter to H^+ reduction and cathodic decomposition. The amount of metal deposited in metal-salt-containing solution is calculated by coulometry ($Ag^+ \rightarrow Ag^0 + p^+$; $Cu^{2+} \rightarrow Cu^0 + 2p^+$) and the coverage Θ is estimated by assuming a close-packed arrangement of the metal atoms.

III. RESULTS

A. Electrochemistry

Presented in Fig. 1 are the current-versus-potential characteristics in the dark of the $x=0.53$ HZT alloy (a) in supporting electrolyte and (b) in metal-salt-containing solution. These characteristics are representative of the results obtained for the whole set of alloys. In case (b), during the negative scan, reduction of Ag^+ and Cu^{2+} ions starts at 0 and -0.2 V versus MSE, respectively, and the Nernst equilibrium potential for a concentration of $5\times10^{-5}M$ is $(-0.108\ V)_{MSE}$ for Ag/Ag^+ and $(-0.430\ V)_{MSE}$ for Cu/Cu^{2+}. The current density measured during reduction of Ag^+ is noticeably larger than for Cu^{2+}.

Figure 1(c) presents the voltammograms of Ag- and Cu-coated electrodes in $0.1M$ $HClO_4$ supporting electrolyte. We observe the existence of an anodic current during the positive scan and of a cathodic current during the negative scan. Such voltammograms remain unchanged even after several potential cycles. This behavior is discussed in the next section of this paper, but we must mention now that these currents correspond to an oxidation of the metal deposit and to the reduction of this oxide, respectively. The latter reaction does not take place if the former does not exist. Such reactions must be avoided during the performance of ER experiments done at fixed dc potential with a superimposed 0.5-V ac modulation; thus the applied dc potential is never positive of $(-0.65\ V)_{MSE}$.

The capacitive behavior versus potential of coated electrodes (not represented here) does not correspond to a classical Mott-Schottky plot. We nevertheless observe that the capacity value becomes larger and larger with in-

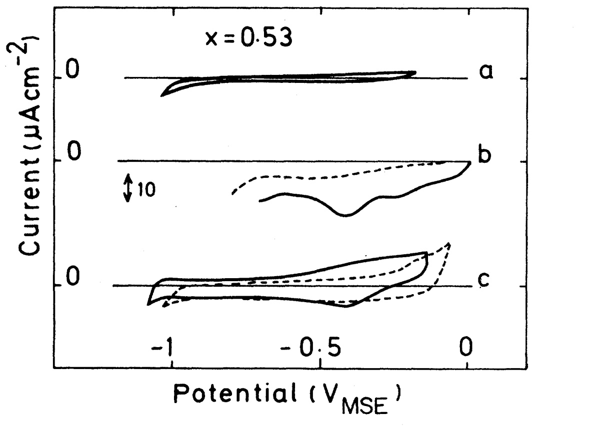

FIG. 1. Current-potential characteristics of $Zn_{0.53}Hg_{0.47}Te$ alloy (a) in contact with $0.1M$ $HClO_4$, (b) in $5\times10^{-5}M$ $AgNO_3$ (——) and $5\times10^{-5}M$ $CuSO_4$ (– – –) containing solution, and (c) Ag-(——) or Cu-(– – –) coated $Zn_{0.53}Hg_{0.47}Te$ in $0.1M$ $HClO_4$. Sweep rate 10 mV s^{-1}.

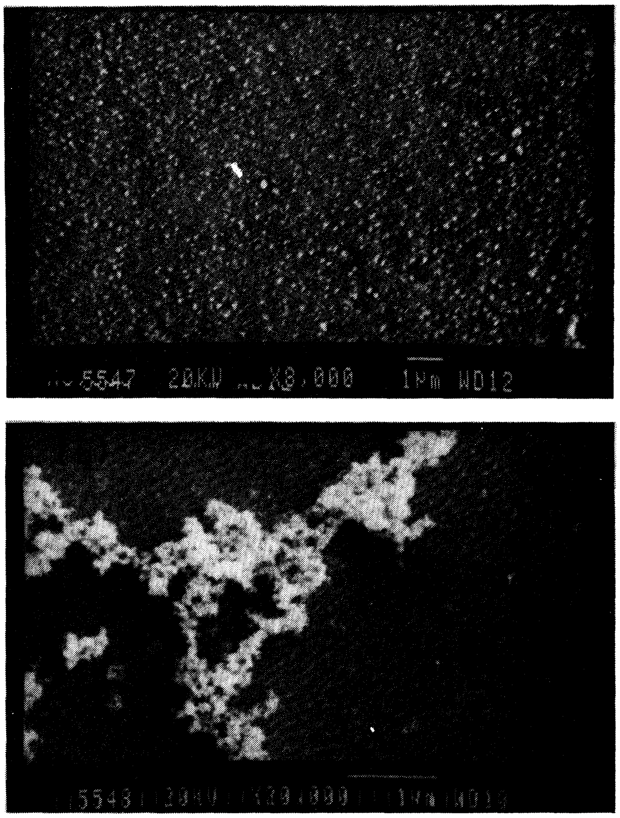

FIG. 2. Scanning electron micrographs of $Zn_{0.53}Hg_{0.47}Te$ coated with Ag submonolayer deposited during 15 s at (a) $V_a = -0.4$ V and (b) $V_d = -0.7$ V.

creasing metal coverage and tends to values obtained with metal electrodes. It seems reasonable to correlate this observation with the increase of the cathodic current in the negative-potential region as shown in Fig. 1(c).

Presented in Fig. 2 are scanning electron micrographs of HZT ($x = 0.53$) coated with Ag deposited at $V_d = (-0.4\ \text{V})_{\text{MSE}}$ and $(-0.7\ \text{V})_{\text{MSE}}$ for 15 s. The morphologies of the deposits are drastically different. While the deposit made at $(-0.4\ \text{V})_{\text{MSE}}$—whose calculated coverage is $\Theta \sim 0.15$—is homogeneous, the deposit obtained at $(-0.7\ \text{V})_{\text{MSE}}$ ($\Theta \sim 0.5$) exhibits some coalescence and nucleation phenomena. At first glance, the influence of V_d on the deposit morphology appears to be different than what has been reported recently about the deposition of Pt on GaAs.[15] In this case, it was noted that the size of the crystallites decreased with decreasing V_d.

B. Electroreflectance

The influence of metal deposits on ER spectra can be observed for the whole series of HZT alloys. However, we present here only the most remarkable results.

Figures 3 and 4 present the spectra obtained with electrolyte-M-HZT (M = Ag or Cu) structures for $Hg_{1-x}Zn_xTe$ with $x = 0.72$ and 0.53, respectively. We also report, for comparison, ER spectra recorded with

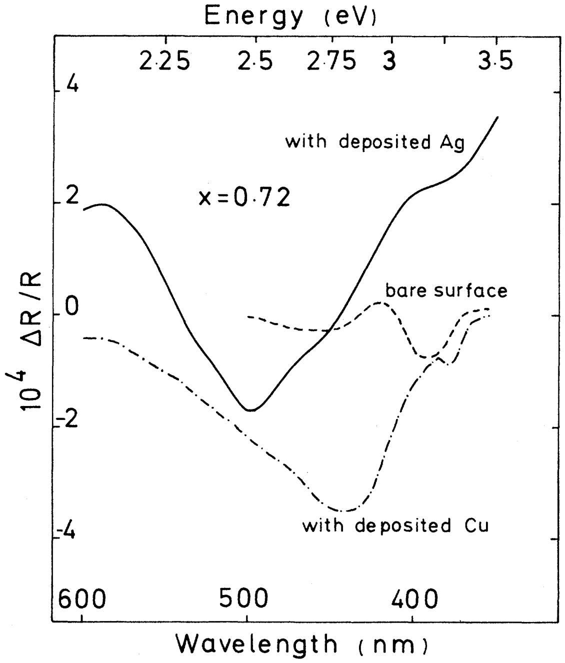

FIG. 3. Influence of Cu (—·—·—·) and Ag (——) submonolayers on the electroreflectance spectrum of a $Zn_{0.72}Hg_{0.28}Te$ electrode. The spectrum relative to the bare surface (— — —) is reported for comparison.

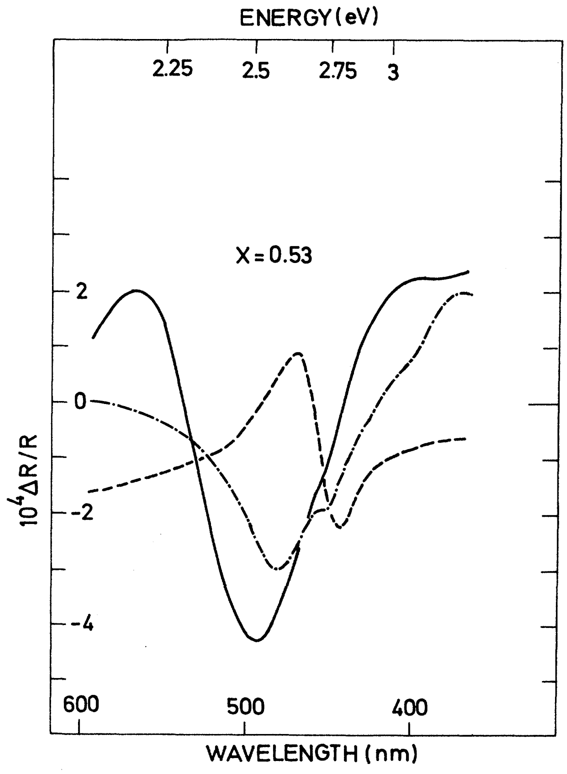

FIG. 4. Electroreflectance spectrum of a $Zn_{0.53}Hg_{0.47}Te$ surface without (— — —) and with Cu (—·—·—·) and Ag (——) submonolayers.

bare HZT electrodes; they show the characteristic oscillation due to the E_1 (Λ_3-Λ_1) transition. E_1 values and the associated broadening parameter Γ are determined using the three-point method.[16] We obtain, for $x=0.72$,

$$E_1=3.07 \text{ eV} \quad \text{and} \quad \Gamma=200 \text{ meV} ,$$

and for $x=0.53$,

$$E_1=2.71 \text{ eV} \quad \text{and} \quad \Gamma=130 \text{ meV} .$$

The existence of a metal deposit of Cu or Ag drastically decreases the magnitude of the E_1 oscillation, and a new broad feature takes place in the energy range 2.5–2.8 eV for $x=0.72$ and 2.4–2.6 eV for $x=0.53$. We notice that the shape of this new spectrum depends on the deposition conditions, i.e., on the microstructure of the metal deposit. This is shown in Figs. 5 and 6, where the evolution of the ER spectrum obtained with HZT ($x=0.53$) as a function of the deposition time t_d for two different deposition potentials V_d [$(-0.4 \text{ V})_{\text{MSE}}$ and $(-0.7 \text{ V})_{\text{MSE}}$] is represented. We observe that when the deposition potential is close to the onset potential of the reduction of M^+ into M^0, the magnitude of the spectrum is larger than when V_d is more negative. Further, when t_d increases, the energy of the minimum in the ER spectrum shifts slightly towards lower energies. Last, we must emphasize the fact that the broad ER feature due to metal deposits remains unchanged even after several scans in the potential range [$(-0.2 \text{ V})_{\text{MSE}}$ to $(-1.1 \text{ V})_{\text{MSE}}$]. When the coverage becomes higher than a monolayer, the magnitude of the minimum decreases rapidly, and finally the spectrum disappears totally; at the same time, we observe that the electrode surface becomes dull. Although the broad ER feature mentioned previously is obtained only for some of the alloy compositions ($x=0.72$, 0.53, and 0.33) that were available, it seems reasonable to assume its existence between the two extreme limits of this composition range. But for $x=0.16$, 1 (ZnTe), and 0 (HgTe), the existence of a metal deposit induces only a small deformation of the E_1 oscillation, together with a shift of the baseline of the spectrum. A similar observation has been done with GaAs, a III-V compound whose ionicity is much lower than that of ZnTe and likely of HZT as well.[17]

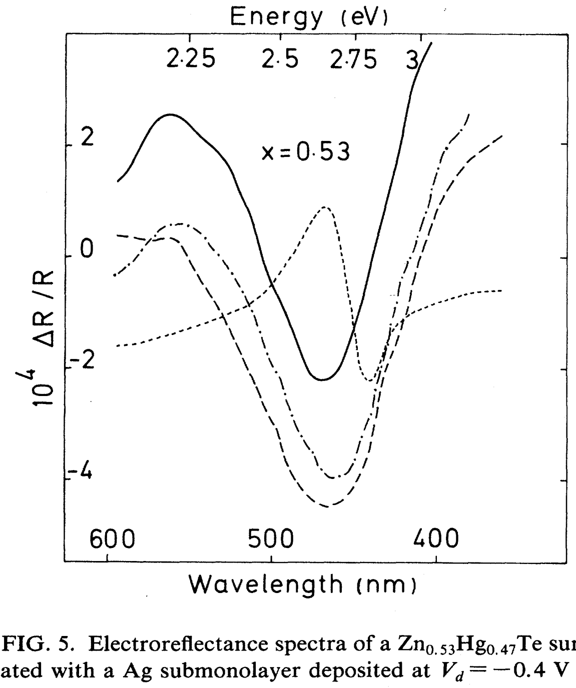

FIG. 5. Electroreflectance spectra of a $Zn_{0.53}Hg_{0.47}Te$ surface coated with a Ag submonolayer deposited at $V_d=-0.4$ V during different time t_d: 30 s (– –), 45 s (–·–), and 75 s (——). The spectrum relative to the bare surface is also represented (· · · ·).

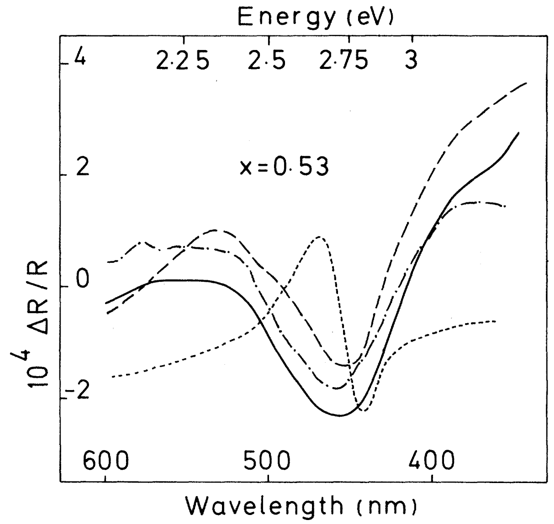

FIG. 6. Electroreflectance spectra of a $Zn_{0.53}Hg_{0.47}Te$ alloy $V_d=-0.7$ V: $t_d=$ 10 s (– –), 15 s (–·–·), 30 s (——), bare surface (· · · ·).

IV. DISCUSSION

As already noted in Sec. III A (Fig. 1), electrochemical Ag and Cu deposition in the dark occurs at potentials more positive than the equilibrium Nernst potentials [$(-0.108 \text{ V})_{\text{MSE}}$ and $(-0.430 \text{ V})_{\text{MSE}}$ for Ag^+/Ag^0 and Cu^{2+}/Cu^0, respectively, with a concentration of $(5\times10^{-5})M$]; that is, before bulk deposition can take place. By analogy with what is observed at metal substrates,[12(b)] where this phenomenon is called "underpotential deposition," we can suppose that in this regime a metal monolayer is formed whose coverage is varied by means of the electrochemical conditions of the experiment.

The electrochemical mechanism is tentatively explained in Fig. 7. The location of the band edges of the HZT alloy on the potential scale is such that the thermodynamic free energies of the two redox systems (Ag^0/Ag^+ and Cu^0/Cu^{2+}) are lower than the top of the valence band of HZT. Reduction of metal cations M^+ can thus occur by injection of holes from M^+ into the HZT valence band according to

$$M^+_{\text{sol}} \rightarrow M^0_{\text{ads}} + p^+_{\text{VB}} ,$$

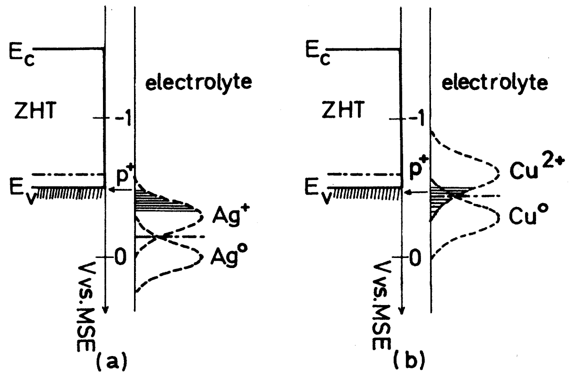

FIG. 7. Energy diagram of $Zn_xHg_{1-x}Te$ in contact with electrolyte containing redox systems Ag^+/Ag and Cu^{2+}/Cu. The energies of these redox systems are calculated thermodynamically.

where the subscripts sol, ads, and VB indicate that the species are in the solution, adsorbed, and in the semiconductor valence band, respectively.

Once the Ag (Cu) deposit is done on the semiconductor surface, the HZT electrode presents an extraordinary behavior when studied again in the supporting electrolyte, and electrochemistry and electroreflectance provide convenient *in situ* tools for the investigation of the new interface which has been created.

In electroreflectance, two features appear to be of particular importance: (i) the decrease and vanishing of the ER oscillation correlated with the E_1 transition in the HZT substrate, and (ii) the creation of a new broad ER spectrum in correlation with the electrochemical behavior of the metal-covered electrode.

The problem of the vanishing of the E_1 can be treated, most likely, in terms of a Fermi-level-pinning (FLP) process induced by the metal deposition. If, in the present state of our investigation, a quantitative interpretation of the new ER feature appears to be difficult, we can nevertheless assume that it is due to a specific behavior of the new interface corresponding to the metal deposit. Qualitatively we can reasonably assume that the ER signal is, for a metal-coated electrode, a linear combination of two contributions: one originating in the semiconductor and the other in the coated surface. We write

$$(\Delta R/R)_{\rm tot} = a(\Delta R/R)_{\rm SC} + b(\Delta R/R)_M \ , \qquad (1)$$

where a and b are coefficients which depend on the experimental conditions, mainly the deposit structure; $(\Delta R/R)_{\rm tot}$ is the total ER signal, whereas $(\Delta R/R)_{\rm SC}$ represents the response of the semiconductor substrate including surface states and $(\Delta R/R)_M$ that of the metal-coated surface. By introducing interface energy states in the $(\Delta R/R)_{\rm SC}$ term of Eq. (1), the influence of a FLP process on the magnitude of a ER signal can be put in evidence.

In the low-field limit, an assumption which seems reasonable in the case of E_1 transitions, $(\Delta R/R)_{\rm SC}$ can be written[16]

$$(\Delta R/R)_{\rm SC} = (2eN_A/\epsilon_s)\Delta V_{\rm SC} L_{\rm SC}(\hbar\omega) \ , \qquad (2)$$

where $L_{\rm SC}(\hbar\omega)$ is the line-shape function, N_A the ionized acceptor density, ϵ_s the static dielectric constant of the semiconductor, and e the electron charge. $\Delta V_{\rm SC}$ is the part of the modulating voltage in the space-charge region of the semiconductor.

In the absence of interface energy states, we have

$$\Delta V = \Delta V_{\rm SC} \ , \qquad (3)$$

where ΔV is the total modulating voltage. When interface states exist, it is easy to demonstrate that

$$\Delta V_{\rm SC} = \alpha \Delta V \ , \qquad (4)$$

α accounting for the potential drop $\Delta V_{\rm H}$ which takes place in the Helmholtz layer taking into account interface states.[18] If some restrictive conditions are fulfilled,[19] α can be expressed as follows:

$$\alpha = 1/(1 + e^2 N_{\rm SS}/C_H) \ , \qquad (5)$$

where $N_{\rm SS}$ is the density of surface states and C_H the Helmholtz capacity. In the present treatment we consider that C_H remains constant.[20] Therefore, $(\Delta R/R)_{\rm SC}$ depends on the density of interface states, and when $N_{\rm SS}$ increases, $\alpha \rightarrow 0$, a situation that corresponds to Fermi-level pinning and vanishing of the ER signal and that mimics the experimental behavior.

Zur *et al.*[21] have studied theoretically the Fermi-level position at semiconductor-metal interfaces. They have shown that for metal submonolayer coverages, FLP can occur for interface state densities as low as 10^{12} cm^{-2}, whereas for thick metal layers a density of at least 10^{14} cm^{-2} is necessary. According to the unified defect model for semiconductor-metal interfaces,[22] the Fermi-level position at the interface is influenced by the presence of chargeable defects at the semiconductor surface. Since the whole system is electrically neutral, there must be charges that compensate the defects somewhere in the system. For submonolayer coverages, these charges are the shallow impurities in the depletion region of the semiconductor. It seems reasonable to assume that our system corresponds to this configuration, a simple calculation leading to metal coverage ranging between 0.1 and 1 monolayer, whereas micrographs show that the metal deposit leaves large areas free of metal on the semiconductor surface. The effect of the submonolayer metal coverage is to increase the number of chargeable defects (strong metal-HZT interaction) up to a level at which FLP can occur. This statement is supported by the fact that the oscillation corresponding to the E_1 transition of HZT decreases extremely rapidly for very low metal coverages (an inflection point remains at the E_1 energy on the big broad feature) and vanishes completely for larger coverages.

The problem that appears far more complicated is represented by the second term $(\Delta R/R)_M$ in relation (1), which accounts for the new broad feature created by the deposition of Ag(Cu) on HZT. Before discussing this, some remarks are necessary that bring important information about this term to light. First, the magnitude of the spectrum does not appear to be proportional to the modulating voltage. Second, such spectra are totally different from those obtained at solid Cu (Ref. 23) and Ag (Ref. 24) electrodes as well as at semiconductor electrodes. Third, the broad feature typical of metal deposits at HZT electrodes does not exist in the case of coated HgTe, ZnTe, and GaAs, as already observed in the case of Pb deposits at Ge electrodes.[13] Therefore, the chemical composition of the substrate seems to play a prominent role in the observed behavior. These remarks lead to questions about the physical nature of the measured spectra, especially in relation to a derivative of the interface dielectric function.

As long as the metal layer remains transparent or quasitransparent (a situation which corresponds to results in Figs. 3–6), the ER spectra present a characteristic shape. However, this spectrum exists only when there is a metal deposit at the HZT surface, and its shape depends only slightly on the morphology of the deposit but strongly on the chemical composition of the alloy substrate. The biggest effect is obtained for alloys with $0.3 \leq x \leq 0.7$, thus suggesting that there is a strong interaction between substrate and metal coverage which peaks in this composition range. The hypothesis of a chemical interaction between metal and HZT seems supported by observations made previously which have shown that metal deposited (not electrochemically) at II-VI compounds presents a more pronounced chemical interaction with the substrate than in the case of III-V compound semiconductors, probably due to their higher ionicity.[6] Further, the case of metal deposits on HCT, a close parent of HZT, has received special attention,[25] and it has been demonstrated experimentally (mainly by x-ray photoelectron spectroscopy (XPS) that Ag and Cu deposits on cleaved and sputtered substrates lead to interfacial reactions, including formation of Ag and Cu tellurides as well as Hg losses. In the case of HZT substrates coated electrochemically with Ag or Cu, similar interactions and reactions can be postulated, taking into account the existence of the broad feature corresponding to the term $(\Delta R/R)_M$ in Eq. (1) as well as the particular electrochemical behavior of the coated HZT electrodes, even if it is known that HZT is chemically more stable than HCT.[26] Generally, for metal deposited onto metal substrates, the deposit can be desorbed by electro-oxidation during a positive-potential sweep (stripping technique) as is observed experimentally both for Cu (Ref. 27) and Ag (Ref. 28) on various metal substrates. In the present experiments, even after several cyclings in supporting electrolyte in the potential range $[(-0.2\ \mathrm{V})_{\mathrm{MSE}}$ to $(-1.1\ \mathrm{V})_{\mathrm{MSE}}]$, voltammograms of coated electrodes remain unchanged [Fig. 1(c)] and the ER spectra are not modified (Figs. 3 and 4). Due to the absence in the supporting electrolyte of anodic and cathodic current in this potential range [Fig. 1(a)], we can be reasonably sure that the bare HZT electrode is free of oxide and that the metal deposit is made on a clean surface. Those currents observed with coated electrodes [Fig. 1(c)] can be attributed unambiguously to the metal coating. These observations tend to demonstrate that Ag and Cu deposits are not dissolved during the positive polarization, but only oxidized (and not the substrate in the places where it is free of metal), and that these oxides are reduced during the negative polarization.

Therefore, it seems reasonable to assume that Cu and Ag deposits made electrochemically at the HZT electrode would present a particular chemical structure due to a strong interaction with the substrate that leads to a specific electrochemical and electro-optical behavior. As already noticed in Sec. III B in correlation with the shape of ER spectra, this interaction is probably stronger for alloys with $0.3 \leq x \leq 0.7$ than for alloys with composition close to binary compounds. Such a phenomenon could likely be correlated with the disorder existing in the structure of the ternary alloys. This disorder changes with alloy composition and is probably maximum for x between 0.5 and 1, as in the case of HCT alloys.[29]

V. CONCLUSION

The whole set of electrochemical and electro-optical results presented here tends to demonstrate that the surface of mercury-zinc-telluride alloys, covered with a submonolayer deposit of Ag or Cu, behaves very specifically. For the first time, to our knowledge, the creation of an electroreflectance signal completely different from that of the substrate and that directly reflects an interfacial phenomenon linked with metal coating, is reported. Further, the electrochemical behavior of Ag and Cu deposits which do not desorb easily during anodic polarizations appears to be anomalous when compared with what is usually reported at metal substrates. Therefore, it seems reasonable to postulate a strong chemical interaction between Ag and Cu atoms deposited electrochemically and the constituents of the substrate. Even if in the present state of our experiments a complete explanation of the phenomenon is not possible, it seems reasonable to make a parallel with results obtained in solid-state physics concerning the formation of metal-semiconductor contacts, especially in the case of mercury-cadmium-telluride alloys.

Electrochemistry and electrolyte electroreflectance provide a unique set of *in situ* techniques enabling us to investigate the first step of the electrochemical formation of metal-HZT contacts.

Due to drastic changes in the local environment, it is not completely proven that the use of classical means of surface investigation like Auger-electron spectroscopy or x-ray photoelectron spectroscopy would elicit information related to the actual interface existing in the electrolyte. Therefore, complementary studies by spectroscopic ellipsometry or extended x-ray absorption fine structure, which can also be *in situ* techniques, are still desirable to try to answer some questions concerning the optical role of the interface and the chemical interaction between metal and HZT. In the next step of our investigations, we will attempt to elucidate the particular role of Hg in our results, and electrochemical and ER experiments are in progress concerning metal deposits at mercury-cadmium-telluride alloys.

[1] Y. Nakato, T. Ohnishi, and H. Tsubomura, Chem. Lett. No. 8, 883 (1975); Y. Nakato, K. Abe, and H. Tsubomura, Ber. Bunsenges Phys. Chem. **80**, 1002 (1976).

[2] Y. Nakato, K. Ueda, H. Yano, and H. Tsubomura, J. Phys. Chem. **92**, 2316 (1988).

[3] M. Szklarczyk and J. O' M. Bockris, J. Phys. Chem. **88**, 5241 (1984); A. Heller, D. E. Aspnes, J. D. Porter, T. T. Sheng, and R. G. Vadimski, *ibid.* **89**, 4444 (1985).

[4] M. Ludwig, G. Heymann, and P. Janietz, J. Vac. Sci. Technol. B **4**, 485 (1986); R. Reineke and R. Memming, Surf. Sci. **192**, 66 (1987).

[5] See, e.g., L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982); I. Lindau and T. Kendelewicz, C. R. C. Crit. Rev. Solid State Mater. Sci. **13**, 27 (1986).

[6] L. J. Brillson, J. Phys. Chem. Solids **44**, 703 (1983).

[7] R. Triboulet, J. Cryst. Growth **86**, 79 (1988).

[8] B. Toulouse, R. Granger, S. Rolland, and R. Triboulet, J. Phys. (Paris) **48**, 247 (1987).

[9] C. Nguyen van Huong, R. Triboulet, and P. Lemasson, J. Cryst. Growth **86**, 570 (1988).

[10] N. Schevchik, J. Tejeda, M. Cardona, and D. W. Langer, Phys. Status Solidi B **59**, 87 (1973).

[11] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).

[12] R. Adzic, E. B. Yeager, and B. D. Cahan, J. Electrochem. Soc. **121**, 474 (1974); D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering,* edited by H. Gerischer and C. W. Tobias (Wiley, New York, 1978), Vol. 11, p. 125.

[13] A. B. Ershler, A. V. Kaisin, Kh. Z. Brainina, and I. M. Levinson, Elektrokhim. **22**, 203 (1986).

[14] C. Hinnen, C. Nguyen van Huong, A. Rousseau, and J. P. Dalbera, J. Electroanal. Chem. **95**, 131 (1979).

[15] P. Allongue and E. Souteyrand, J. Vac. Sci. Technol. B **5**, 1644 (1987).

[16] D. E. Aspnes, Surf. Sci. **37**, 418 (1973).

[17] C. Falter, W. Ludwig, and M. Selmke, Solid State Commun. **54**, 321 (1985).

[18] P. Lemasson and C. Nguyen van Huong, J. Electrochem. Soc. **135**, 2080 (1988).

[19] R. P. Silberstein, F. H. Pollak, J. K. Lyden, and M. Tomkiewicz, Phys. Rev. B **24**, 7397 (1981).

[20] S. Licht and V. Marcu, J. Electroanal. Chem. **210**, 197 (1986).

[21] A. Zur, T. C. McGill, and D. L. Smith, Phys. Rev. B **28**, 2060 (1983).

[22] W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, J. Vac. Sci. Technol. **17**, 1019 (1980).

[23] R. Kotz and H. J. Lewerenz, Surf. Sci. **97**, 319 (1980).

[24] J. D. E. McIntyre, *Advances in Electrochemistry and Electrochemical Engineering,* edited by R. H. Müller (Wiley, New York, 1973), Vol. 9, p. 61.

[25] For a recent review on metal-HCT junction formation, see, e.g., G. D. Davis, W. A. Beck, M. K. Kelly, D. Kilday, Y. W. Mo, N. Tache, and G. Margaritondo, Phys. Rev. B **38**, 9694 (1988), and references therein.

[26] A. Sher, M. A. Berding, M. Van Schilfgaarde, A. B. Chen, and R. Patrick, J. Cryst. Growth **86**, 15 (1988).

[27] S. H. Cadle and S. Bruckenstein, Anal. Chem. **43**, 1858 (1971); W. J. Lorenz, J. Morentzio, and E. Schmidt, J. Electroanal. Chem. **33**, 12 (1971); C. Nguyen van Huong and M. J. Gonzalez-Tejera, *ibid.* **244**, 249 (1988).

[28] G. W. Tindall and S. Bruckenstein, Electrochim. Acta **16**, 245 (1971); E. Schmidt and S. Stucki, J. Electroanal. Chem. **39**, 63 (1972).

[29] L. Viña, C. Umbach, M. Cardona, and L. Vodopyanov, Phys. Rev. B **29**, 6752 (1984).

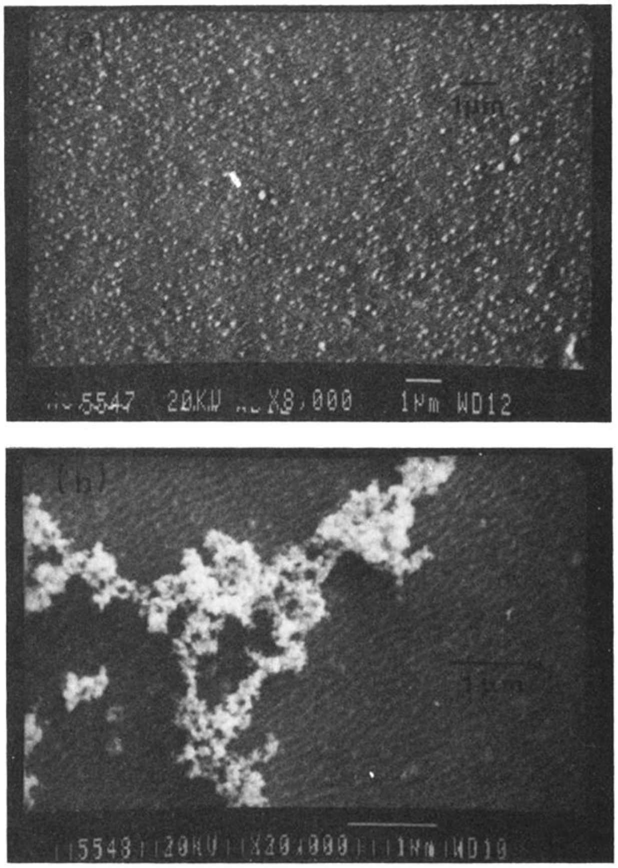

FIG. 2. Scanning electron micrographs of $Zn_{0.53}Hg_{0.47}Te$ coated with Ag submonolayer deposited during 15 s at (a) $V_a = -0.4$ V and (b) $V_d = -0.7$ V.