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Photoelectrochemical effect of the anodic oxide of $Hg_{1-x}Cd_xTe$[a]

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Two aspects of the electrochemical behavior of $Hg_{1-x}Cd_xTe$ in anodizing solution are presented. The current-voltage relationship for anodically oxidized $Hg_{1-x}Cd_xTe$ under cathodic bias has been examined and found to be independent of film thickness or substrate composition and carrier type for oxides exceeding 100 Å thick. For samples in solution biased anodically, ultraviolet light absorption results in increased electrode current. Mechanisms for these effects are discussed.

The anodic oxide of $Hg_{1-x}Cd_xTe$ (HCT) is of practical importance in the fabrication of devices which are based on this material.[1,2] Even when the passivation layer on the HCT is not solely the anodic oxide, knowledge of its properties and the properties of the HCT-oxide interface is desired. Therefore, this oxide has recently been thoroughly investigated with respect to its composition,[3,4] mechanism of growth,[5,6] and electronic properties.[7,8] It is the aim of this communication to describe and to discuss the implications of some of the properties of the anodic film of HCT which can be observed *in situ* (while the oxidized HCT is still immersed in the anodizing solution) and which are relevant to its role as a passivating and insulating agent, namely, its current-voltage characteristics and its photoelectrochemical behavior.

In these experiments, anodic oxides were potentiostatically grown to different thicknesses on HCT substrates of various compositions which were etched in 1% bromine methanol prior to insertion in solution or cleaved in the anodizing mixture.[9] Anodization was performed in 0.1-M KOH, 90% ethylene glycol solution. The drop in formation current of the oxide to a value nearly constant with time was taken as an indication that the oxide film had reached its final thickness for a given voltage (≈ 50 Å/V for potentials greater than 0.6 V versus the Hg/HgO 0.1-M KOH reference electrode used in this work[9]). To examine the reduction processes important in MCT anodic systems, the electrode potential was then scanned linearly in the negative direction with respect to the reference electrode and the current monitored as a function of voltage. In a second experiment, the photoelectrochemical response of the oxide films in solution was studied by monitoring the change in dc current flowing through positively biased oxidized HCT electrodes as a function of electrode illumination. For this purpose, ultraviolet light from a mercury lamp was dispersed by a Bausch and Lomb monochromator and illuminated the electrode in so-lution (from the oxide side) through a quartz window. Light fluxes of the order of 5×10^{13} photons $cm^{-2} sec^{-1}$ were incident in this way.

The MCT electrode current response to the negative potential scan is shown in Fig. 1 for oxide films initially formed to different thicknesses on two substrates. While the anodic oxide can withstand positive potentials up to 20 V without giving rise to appreciable electronic currents (e. g., OH^- oxidation), its potential scan in the negative direction is limited by the electrochemical reactions which correspond to the oxide reduction[6] and which can be considered as electron emission into electron acceptor levels in solution.[10] Similar "rectification" properties of anodic films in solution have been observed before[11] and reflect the existence of energy barriers for free-carrier transport at either the HCT-oxide or the oxide-electrolyte interface. Information regarding the reduction reactions is obtained from the current behavior corresponding to negative potentials [Fig. 1(a) and (b)]. The current-voltage characteristics of anodic oxides grown to the same potential on either p or n substrates are similar. Very thin films (formed at 0.5 V) are reduced at an onset potential which roughly corresponds to the thermodynamic threshold for their reduction.[6-9] Thicker films exhibit an increasingly higher over voltage for reduction which for thick enough

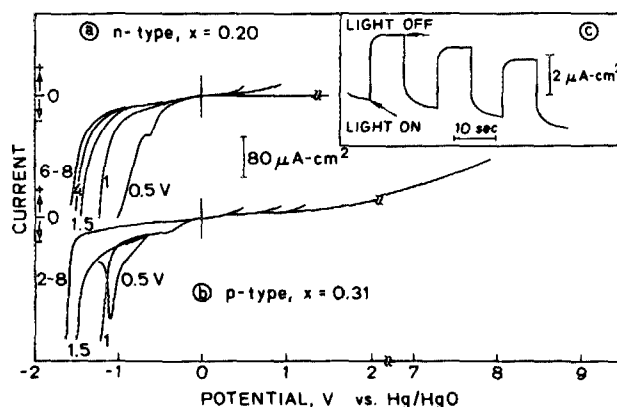FIG. 1. (a) and (b): Current-voltage curve for oxide films grown on HCT. The formation potential of the film is indicated near the curves. (c): Photocurrent of a 250-Å- thick anodic oxide film grown on HCT (solution: 0.1-M KOH in 90% ethylene glycol; illumination: white light).

films (approximately 100 Å on the p-type sample) becomes independent of film thickness. These observations suggest that the cathodic current is mainly controlled by the mechanism by which electrons are injected from the HCT into the oxide rather then by the availability of electrons at the HCT surface (which should differ for an n or p substrate) or by the conduction mechanism within the "bulk" of the oxide. The nature of the HCT-oxide electrical contact is not clear. Even at a "blocking" contact[12] electrons can nevertheless be emitted from the HCT into the oxide by tunneling or Schottky emission[13] provided the electric field at the interface is sufficiently high. Further, it seems plausible that mobile cations in solution (e. g., K^+) would penetrate the oxide and be driven toward the HCT-oxide interface where they would produce a positive space charge region which narrows the energy barrier and by this facilitates the electron transfer through the barrier.[14] These positive ions, when present in the oxide at a high concentration, could also create impurity bands which would provide a conduction route for electrons from the HCT to solution.[15] The effect of these current sources should be insensitive to film thickness and to substrate doping provided that the thermal generation rate of electrons at room temperature in the p-type HCT is fast enough to sustain an inverted surface. The reason that such "breakdown" of the oxide under positive gate bias is not observed in solid-state MOS devices which employ the HCT and its oxide is not clear, but may be related to the relatively small value of film thickness used here, to the fact that the measurements were done at room temperature rather than at liquid-nitrogen temperature, or to the contribution of ions from solution and/or to the consumption of the oxide during the passage of the cathodic current.

In the curves in Fig. 1, a small current is observed for anodic potentials and arises mainly through ionic dissolution of the HCT constituents. Electronic oxidation currents are prohibited because of the difference in energy between the Fermi level of the oxide and the so called "Fermi level in solution,"[16] which corresponds to the energy level of electrons of the redox couple. This energy difference results in the formation of a solid-liquid junction energy barrier for the transfer of electrons from solution to the oxide.[17] The anodic current increases when a positively biased oxide electrode is illuminated in solution with ultraviolet light of appropriate wavelength.

The current response to illumination changes is shown in Fig. 1; the photocurrent (the difference is current with and without illumination) remains constant for as long as the effect is probed, indicating that the photocurrent consists of a charge transfer across the oxide-electrolyte interface rather than a photoinduced capacitive charging transient. The spectral response of the photoeffect is shown in Fig. 2 where the photocurrent at each wavelength was normalized to the light intensity as measured by a calibrated Cs_3Sb cell[18] (uncorrected for substrate reflectivity). The wavelength dependence indicates the photoeffect is related to the formation of an electron hole pair within the oxide as shown schematically in the band diagram in Fig. 2. The "tailed" appearance of the spectral response is characteristic of the photoresponse of amorphous or very thin materials where the band edges
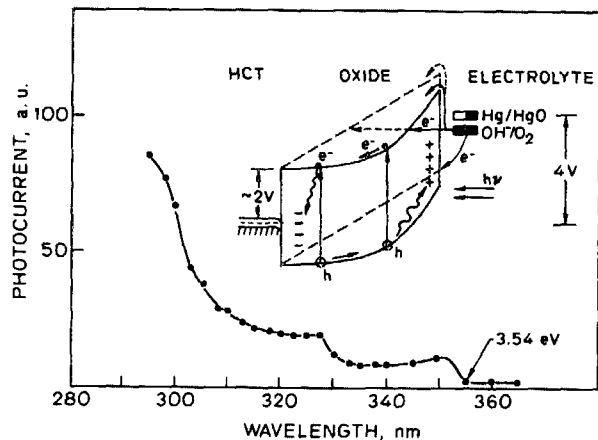

FIG. 2. (a): Spectral response of the photocurrent of a 400-Å anodic oxide on n-type HCT, x = 0.2. Solution as in Fig. 1. (b): Schematic representation of band diagram and photoprocess at an HCT oxide electrode biased to 4 V (vs Hg/HgO reference electrode) under illumination and in the dark (dashed lines).

are not well defined.[19] The oxide band gap can be evaluated from the wavelength corresponding to the onset of the photocurrent and was found to be 3.54 eV in agreement with other determinations.[7] A negative photocurrent was observed when a negative biased (− 1.2 V) oxide electrode was subjected to visible illumination ($\lambda < 5000$ Å). This photocurrent can be attributed to photoemission of electrons from the substrate into the conduction band of the oxide[7] and will not be considered here.

In many materials,[20–27] photocurrent from positively biased electrodes has been attributed to the injection of photogenerated holes from the valence band of the oxide into the appropriate level in solution, resulting in oxidation of the solution or decomposition of the oxide. In the case of the HCT oxide, photocurrent may also result from an additional mechanism discussed below. In these experiments, the penetration depth of the exciting light (for which an absorbtion coefficient of about 10^5 cm^{-1} is assumed) exceeds the thick-
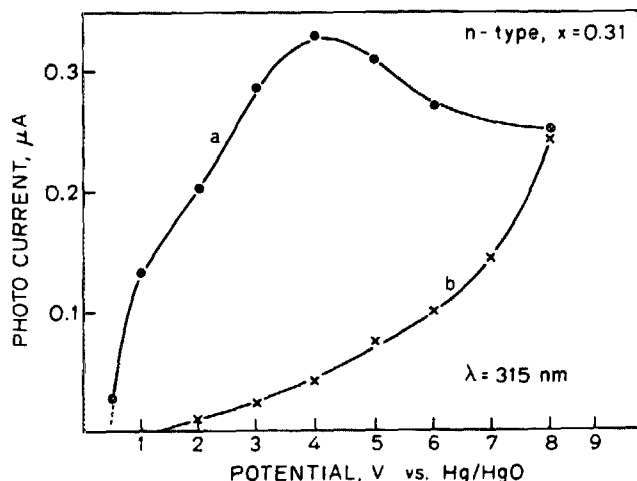

FIG. 3. (a): Dependence of photocurrent on oxide thickness $\approx$ 50 Å/V. (b): Dependence of photocurrent on electrode potential for an oxide film grown at 8 V on n-type HCT, x = 0.31. [Solution as in Fig. 1(c); illumination: $\lambda = 3150$ Å.]

ness of the thickest film employed (≈ 400 Å). Therefore, the number of free carriers collected and the observed photocurrent should increase as the film thickness increases. Instead, as shown in Fig. 3(a) the photocurrent peaks for films grown at 4 V (≈ 200 Å), with a quantum efficiency of about 12%. The decrease in the efficiency of the process suggests that either the photoelectrochemical properties (e.g., lifetime of excess free carriers) of the film deteriorate as its formation potential increases or that the main contribution to the photocurrent is due to carriers produced near the oxide boundaries rather than in the interior of the film. The first possibility is related to the fact that the oxidation state of anodic films increases at higher formation potentials[28] and the fully oxidized anodic films were found to have inferior photosensitivity compared to partially reduced films.[21] The second possibility, that the contribution is the current produced at the oxide boundaries, is related to a mechanism for the photocurrent alternative to hole injection into solution and is shown schematically in Fig. 2. Instead of being injected into solution, photogenerated holes are trapped near the oxide-electrolyte interface resulting in a positive space-charge region which modifies the band bending of the oxide to a situation more favorable for electron emission from solution. This mechanism is supported by the dependence of photocurrent on field within the oxide. Figure 3(b) reproduces the photocurrent measured at various electrode potentials for an oxide film formed at 8 V (≈ 400 Å). Consistent with the picture of electron emission given above, the photocurrent is observed in this case to increase nonlinearly and shows no limiting behavior.

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