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HIGH SENSITIVITY OPTICAL MODULATED OPTICAL AND RAMAN  
INVESTIGATION OF GAAS AND ITS OXIDES(U) BROOKLYN COLL  
NY DEPT OF PHYSICS F H POLLAK 1983 N00014-78-C-0718

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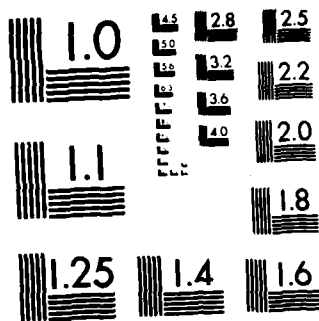
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FINAL REPORT

HIGH SENSITIVITY OPTICAL, MODULATED OPTICAL AND RAMAN  
INVESTIGATION OF GaAs AND ITS OXIDES

ONR CONTRACT # N00014-78-C-0718

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## I. OBJECTIVES

The original purpose of this research program was to investigate the anodic oxidation process in GaAs utilizing sensitive optical techniques. The nature of surfaces in the preparation of semiconductor devices has been a concern of long standing. In particular, the increasingly important role played by GaAs in the fabrication of semiconductor devices suggested the need for a more fundamental understanding of its surfaces. Recently, considerable interest has been shown towards oxidation from the viewpoint of application of surface passivation, planar technology and fabrication of MOS field effect transistors.

Our initial study of the anodic oxidation process in GaAs led to a broader investigation of the properties of the semiconductor-electrolyte interface. In particular, we found new applications of electrolyte electroreflectance (EER) to gain information about this important interface. This work has led to the development of EER as a technique to study surface potential distribution (including flat-band and Fermi-level pinning), optical determination of electrical properties, etc.

## II. RESULTS

### A. Anodic Oxidation in GaAs

We have used a rotating light-pipe reflectometer (RLPR) for the in situ optical study of anodic oxide films on GaAs during their growth and dissolution. Different stages in the oxidation process can be easily identified, including electro-etching, island formation, uniform film growth, and oxide dissolution. The film thickness can be calibrated interferometrically in situ. The dissolution curve is used to determine the dissolution rate as a function of oxide thickness. In addition, the RLPR is used to measure the spectral dependence of the reflectivity of anodized GaAs in situ. Using the reflectivity expression for a three-layer system (i.e., GaAs, oxide, electrolyte) we have been able to fit our data using the previously measured optical constants of

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the oxide.

An example of the use of the RLPR to study oxide growth and dissolution in situ is given in Fig. 1. Here we show the relative change in reflectance,  $R/R_0$ , as a function of time for  $i = 4500 \text{ A}$ . We define  $R/R_0 = (R(d) - R(0)) / R(0)$  where  $R(d)$  is the reflectivity of the sample with an oxide layer of thickness  $d$ , and  $R(0)$  is the reflectivity of the oxide-free substrate, both quantities measured in the electrolyte. The first section of the curve corresponds to the growth of an oxide layer using a constant current density of  $150 \text{ A/cm}^2$ . If the initial portion of the curve is examined in detail, it is found that a period of slower change in  $R/R_0$  occurs, which is due to the initial formation of oxide islands on the substrate. When the voltage across the electrochemical cell rises to 107 V, the current is abruptly shut off and the oxide allowed to dissolve in the open circuit condition. The thickness of the film can be evaluated in situ, since each half-oscillation of the curve indicates a thickness change  $d = \lambda / 4n_{\text{ox}}$ , where  $n_{\text{ox}} = 1.8$ , the refractive index of the oxide over most of the visible spectrum.

Within seconds after the current is shut off, the film starts to dissolve and the interference fringes which occurred during growth are followed slowly in reverse order until all of the oxide has dissolved. A permanent change in reflectance,  $R/R_0 = -2\%$  can be observed in the dissolution curve which is probably the result of slight etching of the surface in this particular sample. It is significant, however, that over the long time interval required for dissolution, all the interference fringes are repeated in reverse order. Except for the brief period close to the start of dissolution, the dissolution rate appears to be constant. These observations indicate that for this set of experimental conditions, oxide growth and dissolution are steady and well-controlled processes which can enlarge the scope of our electroreflectance measurements.

We have investigated the electrolyte electroreflectance (EER) spectra

of N-GaAs in the vicinity of the  $E_0$  transition (direct gap at  $k = 0$ ). A pronounced interference phenomenon sensitive to the dc bias electric field has been observed which we identify with an exciton quenching effect within the semiconductor space-charge region (SCR). We have utilized this excitonic feature to interferometrically probe the dynamic and steady-state properties of the SCR during electrochemical anodization procedures. The same EER spectra also exhibit Franz-Keldysh oscillations, the period of which is explicitly dependent on the ac electric field. Using these phenomena we have shown that the interfacial and oxide electric fields under steady-state conditions are just as sufficient to continue growing the oxide in compensation for slow dissolution. If the dc bias voltage is suddenly reduced, the SCR temporarily collapses due to transient effects which we attribute to very slow interface states in the oxide. These techniques are applicable to the study of the SCR in a variety of semiconductor-electrolyte systems as well as in the Schottky barrier configuration.

#### B. Electrolyte Electroreflectance Study of the Semiconductor-Electrolyte Interface

As a test of some of the above observations on the anodic oxidation of GaAs, EER spectra were measured for single crystal n - CdSe in a polysulfide (Na)H/S = /S) electrolyte. This is a very well characterized system that has been studied extensively for solar cell applications and represents a prototype semiconductor/electrolyte system. Variations of the lineshape as a function of potential were observed. As the potential was reduced below the flatband potential, the electroreflectance signals changed sign. The potential at which this change occurs correlates well with the turn-on potential for light-induced photocurrent and with the intercept of the Mott-schottky plot.

We have investigated the low-field EER spectra of matte polycrystalline electrodeposited N-CdSe in the vicinity of the  $E_0$  (A,B) transitions (direct gap at  $k = 0$ ). Utilizing the properties of low-field EER, we have studied

the distribution of the applied ac voltage in situ in the photoelectro-chemical solar cell configuration: (1) By measuring the in-phase and quadrature EER signals as a function of modulation frequency  $f$ , we have determined the electrical impedance  $Z(f)$  of the interface for  $10\text{Hz} \leq f \leq 10\text{kHz}$ , at the focus of the incident light. These results are in substantial agreement with direct electrical measurements. (2) By measuring the EER amplitude as a function of applied dc bias voltage, we have found evidence for surface states which contribute to Fermi level pinning; similar evidence was not observed for single-crystal CdSe. These techniques are of general applicability for other semiconductor interfaces with optically transparent junctions, and are well suited to topographical scanning.



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