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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 17,7/92	3. REPORT TYPE AND DATES COVERED Final 1 Aug 86 - 31 Aug 89	
4. TITLE AND SUBTITLE Study of Surface Behavior in Function of Temperature of the Quaternary System (Hg,Cd,Zn)Te		5. FUNDING NUMBERS DAAG 03-86-K-0131	
6. AUTHOR(S) James W. Garland (due to the untimely death of Paul M Raccah, the Principal Investigator)		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Illinois at Chicago Department of Physics P.O. Box 4348, M/C 273 Chicago, IL 60680		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 23662.7-EL	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211		11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The work performed under this contract represents an extension of our past work on mercury cadmium telluride (MCT). Under this contract we have focussed on the use of spectroscopic ellipsometry (SE) and the development of new theoretical and analytical tools for the analysis of SE data. Our major achievement was the demonstration of an excellent, physically understandable correlation between the low-temperature dark storage time of MIS devices built on bulk MCT samples and a parameter measured by room-temperature electrolyte electroreflectance (EER) on those samples. The analysis which led to this result required the input of SE data obtained under this contract as well as the EER data. The other experimental results obtained under this grant were the determination of the nature of the broadening of critical-point transition energies in semiconductor alloys and compounds and SE measurements of critical-point energies and of the thickness of the ZnSe epilayers for ZnSe/GaAs heterojunctions. Theoretical and analytical work performed under this contract included the determination of the origin of the quasiperiodic oscillations in numerically differentiated SE data, a procedure to minimize those oscillations, the development of a method to obtain more accurate values of critical-point energies and linewidths from SE data, and the initial work on the development of a greatly improved model for the optical dielectric function.			
14. SUBJECT TERMS spectroscopic ellipsometry, lineshape, optical dielectric function, MIS devices, dark storage time, linewidth, HgCdTe		15. NUMBER OF PAGES 7	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

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INTRODUCTION

This contract initially was proposed largely as a follow-up to the work done on $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ in collaboration with and monitored by the Night Vision Laboratory of the Army under DARPA contract #DAAK70-83-K-0047. It was proposed and initially approved as a study of the variation of the E_c critical-point energy and of the surface properties of the quaternary system $(\text{Hg,Cd,Zn})\text{Te}$ as a function of temperature and alloy composition. The study was to be carried out using spectroscopic ellipsometry (SE), with a temperature cell described in the final technical report for the aforementioned contract #DAAK70-83-K-0047. The Optical Characterization of Materials Laboratory of the Physics Department of the University of Illinois at Chicago, under the direction of Dr. P.M. Raccach, the Principal Investigator for this contract, was to acquire samples from the Night Vision Laboratory and/or industrial materials growers under contract to the Department of Defense and to characterize those samples. The primary purpose of the proposed study was to obtain the spectroscopic data necessary for the use of SE as an *in situ* guide or control in the growth process for $(\text{Hg,Cd,Zn})\text{Te}$.

During the period of time after this work was proposed, before and shortly after the initial funding of this contract, scientific and technological interest in the quaternary system $(\text{Hg,Cd,Zn})\text{Te}$ fell substantially. In particular, other experimental investigations yielded results counter to the theoretical suggestion that Zn should stabilize $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ against Hg vacancies and diffusion. It is the understanding of the author of this report that Dr. Raccach, probably due to this downturn of interest in the system $(\text{Hg,Cd,Zn})\text{Te}$, was not able to secure samples over the desired range of compositions. In any event, quaternary samples were not obtained and the exact area of research performed under the contract was modified somewhat. However, the basic direction of the research performed remained consistent with the spirit of the original proposal and with the interests of DARPA and the Army. In particular, the work performed under this contract and reviewed in this report was exclusively concerned with SE and was primarily directed at the characterization of mercury cadmium telluride (MCT) in such a way as to aid in the efficient growth of high-quality devices for use in focal-plane arrays for IR detection. Thus, neither the experimental technique involved nor the fundamental purpose of the research were changed, although the immediate purpose of the research was upgraded from aiding in materials growth to aiding in device design and growth.

The first, preliminary stage of work under this contract consisted simply of introducing a new student to the spectroscopic ellipsometer and upgrading that instrument. The first project carried out was

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the use of SE to obtain extra information on a series of MCT samples from Texas Instruments (TI), which were also studied by electrolyte electroreflectance (EER). The use of SE as well as EER was crucial in the interpretation and analysis of the EER data and allowed us to show an almost exact, theoretically meaningful correlation between one of the parameters in the EER analysis and the low-temperature dark storage time of MIS devices built on these samples. This work is discussed in detail in paper 2 of this report.

From this work it became clear that obtaining as much information as possible from SE is very important in any optical studies of MCT and other narrow-band-gap semiconductors. Thus, we next investigated five of the primary fundamental problems in the analysis of SE data. Those problems are as follows:

(1) the modification of SE data by even a very thin natural oxide layer, which distorts the optical dielectric function, $\epsilon(\omega)$, obtained from SE data,

(2) the spurious almost periodic component present in the values of $d^2\epsilon/d\omega^2$ and $d^3\epsilon/d\omega^3$ obtained by the numerical differentiation of SE data,

(3) the use of a lineshape which incorporates Lorentzian line broadening in fitting data for which the actual broadening is not Lorentzian,

(4) the fitting of numerically differentiated data with an analytically differentiated line shape, which introduces systematic errors, and

(5) the use of a lineshape which incorporates the critical-point parabolic-band approximation, valid only very near critical-point energies, in fitting SE data.

The investigation of these problems was conducted both experimentally and theoretically and led to papers 1, 3 and 6 in this report, as well as large sections of the Ph.D. theses of H. Abad and C. Kim; methods were developed for the elimination, or at least great reduction, of all but the first of these problems.

Finally, SE was also used under this contract to aid in very important EER studies of ZnSe/GaAs and ZnSe/AlAs heterojunctions. That work is reported in publications 4 and 5 of this report. The next section of this report contains a list of the publications and theses the research for which was supported in part or in whole by this contract and a list of our other relevant publications. The final section summarizes the results obtained under this contract. Copies of the publications supported under this contract are enclosed. Copies of the theses supported under this contract are available upon request.

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**PAPERS AND THESES SUPPORTED IN PART OR IN WHOLE BY
DARPA CONTRACT #DAAL03-86-K-0131**

1. J. W. Garland, H. Abad, M. Viccaro and P.M. Raccah, "Line Shape of the Optical Dielectric Function", Applied Physics Letters, Vol. 52, No. 14, pp. 1176-1178, January 1988.
- *2. P.M. Raccah, J.W. Garland, D. Yang, H. Abad, R.L. Strong and M.C. McNeill, "Evaluation by Room-Temperature Electroreflectance of the 77 K Dark-Storage Time of Bulk Mercury Cadmium Telluride Measured on Metal-Insulator-Semiconductor Devices," Journal of Vacuum Science and Technology, Vol. A7, No. 2, pp.509-516, March/April 1989.
- †3. J.W. Garland, C. Kim, H. Abad and P.M. Raccah, "Determination of Accurate Critical-Point Energies and Linewidths from Optical Data", Physical Review, Vol. B41, No. 11, pp. 7602-7610, April 1990.
- *†4. L. Kassel, H. Abad, J.W. Garland, P.M. Raccah, J.E. Potts, M.A. Haase and H. Cheng, "Study of the Interface of Undoped and p-Doped ZnSe with GaAs and AlAs," Applied Physics Letters, Vol. 56, No. 1, pp 42-44, January 1990.
- *†‡5. L. Kassel, J.W. Garland, P.M. Raccah, M.A. Haase and H. Cheng, "Effects of Zn and Ga Interdiffusion on ZnSe/n⁺GaAs Interfaces" Semiconductor Science and Technology, Vol. 6, No. 9a, pp. A146-A151, September 1991.
- †‡6. C. Kim, J.W. Garland, H. Abad and P.M. Raccah, "Modeling the Optical Dielectric Function of Semiconductors: Extensions of the Critical-Point Parabolic-Band Approximation," Physical Review, Vol. B45, No.20, pp. 11749-11767, May 1992.
- ‡7. Hisham Abad, thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.
- ‡§8. Charles Kim, thesis for the Doctor of Philosophy in Physics, University of Illinois at Chicago, 1991.

* Of the research reported in this paper, only the SE results were obtained under the support of this contract. Those results constituted only a small part of all of the results reported in this paper.

† Due to the severe illness of Dr. Raccah and my unfamiliarity with the distinction between the two contracts, inadvertently this contract was not acknowledged in this paper.

‡ The work reported in this paper (or thesis) was concluded under DARPA contract #N00014-89-J-3165.

§ Some of the work reported in this thesis was supported under DARPA contract #N0014-86-K-0070.

SUMMARY

Our work under this contract has focussed on the use of SE to characterize semiconductor materials and interfaces, unlike the concurrent contracts N00014-86-K-0070 and N00014-87-K-0296, which focussed on the use of EER. The two techniques, SE and EER, are complementary in many respects, and the use of both techniques on the same samples can give information not available from either technique. This is well illustrated by the first material-characterization study performed under this contract. In that study we used SE and EER to investigate a set of 14 very carefully characterized MCT samples. The samples were furnished by the group of Grady Roberts at TI, which had measured the 77 K dark storage time, τ_d , of metal-insulator-semiconductor (MIS) devices built on those samples. The samples chosen covered the entire range of storage times from 6.8 μ s to 190 μ s.

This study was aimed at the qualification of MCT material before device processing, one of the most obvious needs at the production stage. Before this contract and the concurrent DARPA contract N00014-86-K-0070, we had limited our study of MCT materials to p-type materials because n-type materials yielded anomalous spectra which usually could not be well fit using the existing models or fitting functions. Thus, the relationship between our results and device performance had remained indirect. This was the first use of optical measurements to characterize the ability of substrate material to form good MIS junctions.

Despite the fact that n-type materials were at the heart of photoconductor technology and were considered to be of better physical and chemical quality than the p-type materials, our previous results had indicated that the n-type character is largely defect induced. In the course of this study we were led to recognize that not all parts of bulk MCT crystals have equivalent optical and electrical properties. This is because of the high density of defects that affect optically and electrically finite microscopic regions of the material. In particular, the termination of extended defects at the surface leads to a highly polarizable region along the defect. In any model which incorporates the presence of defectuous regions with a high electric or piezoelectric susceptibility, EER spectra must be viewed as the superposition of spectra from bulk and defectuous regions, with the magnitude of the broadening parameter, Γ_s , for the spectrum from the defectuous regions being directly related to the additional defect density in those regions.

The use of such a model allowed us to fit accurately our spectra for the first time, but almost doubled the number of fitting parameters. This much of an increase in the number of fitting parameters made our fitting procedure at best very lengthy and only very slowly convergent and at worst totally

ambiguous; thus, it was unacceptable. It was in order to solve this problem that we performed an SE study under this contract. Because there is no electromodulation in SE, the signal from the defectuous regions is not enhanced in SE. Thus, the SE spectrum arises almost entirely from the majority bulk region of the sample, even though almost half of the EER signal emanates from the small defective regions. Therefore, we used the SE spectra to determine the bulk critical-point energies and linewidths. For the bulk contribution to the EER spectra, those parameters were then fixed at the SE values. Also, we performed an SE study to determine the nature of the broadening of the critical-point spectra. As a result of those SE studies and through a series of approximations based on physical arguments, we were able to reduce the total number of fitting parameters for the E_1 and $E_1 + \Delta_1$ critical-points in our EER spectra from 26 to 13, less than the number, 14, in the GFF for only a single type of region.

We found an outstanding correlation between Γ_3 and τ_3 , with Γ_3 given as an analytic function of τ_3 derivable from a simple physical model. This was the first time that room-temperature optical measurements made on unprocessed starting material had been shown to reflect directly the low-temperature performance of devices built on that material. This study is described more fully in publication #2.

As was mentioned in the Introduction section of this report, this MCT study prompted us to investigate several fundamental problems associated with spectroscopic ellipsometric studies in general. The first of these problems, the effect of a thin native oxide surface layer on SE data is well known; however, we found it not to have an important effect on the results obtained for $d^2\epsilon/d\omega^2$ or $d^3\epsilon/d\omega^3$ and hence not to be important for our MCT study. We dealt with this problem by using a computer program to measure the oxide thickness and subtract out its effect on our SE data.

The first of a series of investigations of the functional form of the optical dielectric function, or, equivalently, the EER and SE lineshapes, also was motivated by the MCT study discussed above. This investigation, which also was completed before the MCT study, showed that the proper functional form for the room-temperature Green's function for an electron-hole pair in a semiconductor compound is primarily Gaussian, not Lorentzian, but is primarily Lorentzian for MCT. We showed that the Lorentzian part measures the alloy and macroscopic defect scattering. We also found a simple modification of the analytic Lorentzian critical-point parabolic-band lineshape which accurately mimics the numerical Gaussian and mixed Gaussian-Lorentzian lineshapes.

The second problem, the presence of a spurious almost periodic component in the values of $d^2\epsilon/d\omega^2$ and $d^3\epsilon/d\omega^3$ obtained by the numerical differentiation of SE data, also had been recognized by others but had never been understood. Contrary to the opinions expressed earlier in the literature, we

found that this problem arises from the numerical smoothing and differentiation of any function or data set containing noise, not from a particular experimental problem associated with SE. The process of numerical smoothing and differentiation corresponds to cutting off the high frequency noise, or truncating the Fourier transformed data, which generates a ringing or oscillation at the approximate cutoff frequency. This problem cannot be avoided, but was dealt with in part by improving our technique for numerical smoothing and differentiation, as is described in the thesis of H. Abad, and in part by further reducing experimental noise. This work is described in detail in publication #1.

Another important source of error in past SE studies of optical lineshapes, linewidths and, to a lesser extent, critical-point transition energies was the universal practice of fitting numerically differentiated SE data with analytically differentiated lineshape fitting functions. This is because all the methods of numerical differentiation used for SE data contain some smoothing and hence some broadening. That broadening adds to the true linewidths and distorts the lineshape. We show in detail in publication #3 how this source of error can be eliminated by simultaneously numerically differentiating and smoothing $\epsilon(\omega)$ and an analytic fitting function for $\epsilon(\omega)$, using exactly the same algorithm for both.

Finally, work was started under this contract and completed under DARPA contract #N00014-89-J-3165 on a new model for the optical dielectric function. This model greatly reduces the errors associated with the use of the critical-point parabolic-band approximation and all other approximations used in fitting SE data. It is the first model ever to allow one to fit simultaneously $\epsilon(\omega)$ and its first three derivatives, and it does so with great accuracy. This model and its use are described in publication #6.

Spectroscopic ellipsometry was also used under the support of this contract during its final period and later under the support of DARPA contract #N00014-89-J-3165 in support of EER studies of ZnSe/GaAs and ZnSe/AlAs heterojunctions. It was used in particular to measure the thickness of the ZnSe epilayers and to measure the ZnSe bandgap. This was a small but important part of the overall study of ZnSe/GaAs and ZnSe/AlAs heterojunctions, primarily supported by DARPA contract #N00014-87-K-0296 and later #N00014-89-J-3165. This study revealed the existence of strong interdiffusion of Zn and Ga atoms and of a resultant barrier to electron flow in n-type GaAs buffer layers or substrates. It was of great value to Dr. M.A. Haase of 3M in his development of the first blue-green laser diode. This work is reported more fully in publications #4 and #5.

REPORT OF INVENTIONS AND SUBCONTRACTS

No inventions were made or patent applications filed related in any way to the work performed under this contract. No subcontracts were awarded under this contract.

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